

THE CHEMICAL, MECHANICAL, AND IMPLANT
PROPERTIES OF GLASS-COATED ALUMINA

By

DAVID C. GREENSPAN

A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1977



To Alice

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ACKNOWLEDGEMENTS

The author wishes to express his gratitude to his advisors, E. Dow Whitney, J. J. Hren, R. E. Reed-Hill, and G. Piotrowski for their guidance throughout this work. Special thanks are due to Larry Hench, committee chairman and teacher, for his encouragement and assistance, and for affording the author the opportunity to develop and grow through the course of this project.

He also wishes to thank Ronald A. Palmer and Gary J. Miller for the many hours of helpful discussions and assistance with interpretation of data. In addition, thanks are extended to Marc Weinstein and Steven Bernstein for their technical assistance.

Finally, it is with deepest gratitude and appreciation that the author acknowledges the moral support and editorial assistance of his loving wife, Alice.

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Abstract of Dissertation Presented to the Graduate Council
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

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By

David C. Greenspan

June, 1977

Chairman: Larry L. Hench

Major Department: Materials Science and Engineering

A prosthetic implant system is developed which utilizes a surface reactive glass known to bond to living bone as a coating on high strength, fully dense alumina. Processing procedures which result in bonding of the glass coating to the alumina are established. Electron microprobe studies show a large interfacial zone due to the diffusion of Al ions from the alumina into the glass and alkali ions from the glass into the alumina. This interfacial zone is found to be quite sensitive to the time and temperature at which the glass coating is fired onto the alumina. Methods for processing multiple layers of glass onto the alumina are also developed.

The in-vitro surface reactivity of the glass-coated alumina system in aqueous environments is studied using scanning electron microscopy with energy dispersive x-ray analysis, Auger electron spectroscopy, infrared reflection spectroscopy, and analysis of ions released into aqueous solutions. A range of surface reactivities is found for the various glass-coated alumina systems. The reactivity of the glass-coated alumina is found to be slowed by the presence of Al in the glass coating. The formation of a calcium phosphate film, normally associated with the bone-bonding glass, is found to be inhibited by the presence of alumina in the glass-coated system as well as the bulk glass.

The mechanical properties of the glass-coated alumina are studied using cyclic fatigue testing. The results show a slightly higher endurance limit (at 10^7 cycles) for the glass-coated alumina system over uncoated alumina. The results compare favorably with other works conducted on high purity alumina. In addition to cyclic fatigue testing, lifetime prediction diagrams based on fracture mechanics theory are derived from simple fracture strength vs. stressing rate curves. The results of the stressing rate experiments show that glass-coated alumina has a higher fracture strength than the uncoated alumina. The lifetime diagrams indicate that although the glass-coated alumina has a higher fracture strength, the strength distribution of the

coated alumina is wider than the uncoated alumina. Proof testing is used in conjunction with the lifetime prediction diagrams to insure a given minimum lifetime in service for a constant applied stress. These results are discussed in terms of possible alterations of the material due to processing of the glass coating onto the alumina.

The ability of the glass-coated alumina to form a bond with living bone is investigated using canine femoral and rat tibial models. The reliability of the coated alumina to bond with bone is found to be dependent on the processing history. The mechanical strength of the bone-glass bond is also investigated. The presence of alumina is found to inhibit the bonding of the glass to bone. The observed in-vivo results are related to and found to be consistent with the in-vitro results.

CHAPTER I

INTRODUCTION

The ever increasing use of orthopaedic devices in recent years has led to a major research effort concerned with improving existing materials and developing new and better materials. In addition to the continual work being conducted on metallic implant materials, there has been considerable interest in the possible use of ceramics as prosthetic materials, due to their chemical stability and ability to withstand severe environments.

Much of the early work with ceramics centered around the use of porous materials as a means of attaching load-bearing devices to the skeletal system. It was believed that the porous ceramic would act as a scaffolding and allow tissue ingrowth, thus anchoring the implant to the living tissue. Smith [1] used a mixture of calcium carbonate, alumina, silica, and magnesium carbonate to create a ceramic with an average pore size of 17 μm . This material was impregnated with epoxy to give the ceramic body adequate mechanical strength as an implant material. In-vivo results showed little bone ingrowth into the ceramic.

Hulbert, et al. [2] and Klawitter and Hulbert [3] have investigated porous calcium aluminate for use as a prosthetic material. By mixing calcium carbonate with alumina and firing the pelletized mixture, a structure of interconnected pores was developed. These studies revealed that an average pore diameter of at least 100 μm was necessary to achieve bone ingrowth. Hulbert, et al. [4] have reviewed most of the in-vivo data from various porous ceramics, and conclude that most of these materials show no adverse tissue response, and should be considered for use as bone replacement materials.

More recently, Jecmen, et al. [5], Schnittgrund, et al. [6], and Frakes, et al. [7] have conducted research on the strength of porous ceramic implants, both in-vivo and in-vivtro. In all cases, degradation of strength due to aging occurred. The amount of strength degradation was found to be a function of the volume fraction of porosity in the samples. Generally, a larger strength decrease was found in samples tested after aging in-vivo than in samples aged in physiologic saline solution. The ultimate tensile strength of these materials after aging was found to be less than that reported for human bone [8]. These results raise serous doubts as to whether porous ceramics have tensile strengths high enough for load-bearing situations.

Another approach in the use of porous ceramics has been taken by Heinrich, et al. [9] and Graves, et al. [10, 11]. They used a calcium aluminate ceramic which was found to be totally resorbable (i. e., dissolved by body fluids) in the body. In their approach, the ceramic implant was used to fill space in bony defects. As the implant dissolved, the pore size increased and was gradually filled with mineralizing bone. Presumably, the resulting bone-ceramic structure should act as a composite material maintaining structural integrity and mechanical properties adequate for load-bearing use. Additions of phosphorus to the ceramic (as P_2O_5) appeared to enhance bone formation at the ceramic-tissue interface.

The use of high density alumina (Al_2O_3) has received considerable attention of late. Boutin [12] recently reported on over 500 clinical cases using aluminum oxide ceramic in total hip arthroplasty. This author reported good wear resistance of the material and almost no corrosion of the implants. Griss, et al. [13], in 1973, reported that aluminum oxide ceramics implanted in rat femura were surrounded by a thin fibrous capsule, although there was a noted absence of foreign body reaction. This was attributed to the highly inert nature of the ceramic. Further studies by Griss, et al. [14] showed alumina to have excellent wear resistance and a flexural strength high enough for

use as a load-bearing device. Average flexural strengths of 300-350 MPa were attained. These are similar to values of yield strength reported for various surgical alloys used clinically [15].

Hench, et al. [16-18] have utilized the concept of controlled surface reactivity in designing materials for use in prosthetic devices. A series of invert glasses, called "bioglasses," has been developed which bond to living bone in test animals [19, 20]. Results of these in-vivo experiments have shown intimate contact between the ceramic and implant, with no inflammatory response. More recently, Clark [21] has shown that the chemical characteristics of the implant are important in achieving a bond between the implant and bone. The use of Auger electron spectroscopy to analyze both in-vitro and in-vivo corrosion properties of bioglasses has been reported [22-24]. These results confirm that the controlled surface reactivity of these glasses allows the bonding of the materials to living bone. The major shortcoming of these glasses, however, is their low tensile strength. Housefield [25] reported strengths of approximately 69 MPa (10,000 psi) for a crystallized bioglass ceramic. It is clear that for many orthopaedic problems, the low strength of bioglass would prohibit its use.

It was the objective of this study to show that the bone-bonding properties of the "bioglasses" can be combined with the high mechanical strength of high density alumina in order to create a material which can bond to bone and withstand load-bearing applications. To achieve this end, standard engineering techniques were systematically applied to characterize the in-vitro responses (both chemical and mechanical) of the system. These characteristics were then related to the observed in-vivo response. The results of in-vitro and in-vivo testing were related and compared to the known response of bulk bioglass. In this manner, processing variables could be systematically altered to produce the conditions necessary to achieve intimate bonding of the glass-coated system, while maintaining adequate strength of the system. Hereafter, the terms "single-coated alumina" and "double-coated alumina" will refer to the number of bioglass coatings applied to the alumina substrate.

It is the author's opinion that this type of a systematic approach to materials development has been lacking in the field of biomaterials. It is hoped that this text may serve as a guide for future biomaterials work.

CHAPTER II

DEVELOPMENT OF A DIFFUSIONAL BOND AT THE BIOGLASS-ALUMINA INTERFACE

Introduction

Reactions occurring at a ceramic glaze-body interface have been the subject of study for some time [26, 27]. Some of this work has been directed toward determining the effect of interfacial reactions on glaze fit [28]. It was concluded that reactions occurring at the glaze-body interface could alter the properties of the glaze enough to change the glaze fit. Other researchers have studied the solvent action of glazes on the substrate [29, 30]. The chemical resistance of certain water-soluble glasses has been noted to change when fired onto a ceramic body [31]. This effect was found to be due to the diffusion of ions into the glaze, thereby altering its composition. More recently, the use of glazes to give ceramic ware high strength by the formation of a compressive surface layer has been investigated [32]. From these works it is evident that the reactions occurring at a glaze-body interface are important in development and control of certain physical and chemical properties of the system. Therefore, as

a first step in the development of a bioglass-coated alumina system, it is necessary to accurately detail and control the interfacial reactions between the glass and the alumina substrate.

The early work of Kramer [26] points out that by choosing a glaze with a thermal expansion slightly lower than the body, a compressive surface stress will develop, thereby increasing the strength of the glazed body. This fact has become well established over the years, and is standard practice in choosing the proper glaze for a ceramic body [33, 34]. Platts, et al. [35] and Kirchner, et al. [36] have utilized this principle to increase the flexural strength of high density alumina. The choice of a glass coating composition in the present study, however, must be limited in order to meet biocompatibility requirements as described in the previous section [16-19]. The composition of the alumina body is also severely limited due to strength requirements, as well as the need for a relatively inert substrate material. The selection of these two materials has eliminated the possibility of altering the physical properties of either the glass or alumina to achieve the conventional glass to ceramic bond.

In this chapter is summarized the effect of various firing times, firing temperatures, and the number of coatings on the development of the diffusional bond between bioglass and alumina. It is the object

of this study to establish processing procedures which will allow bonding of the glass-alumina interface without compromising the biocompatible properties of the bioglass or the mechanical strength of the alumina. By systematically altering the firing times, firing temperatures, and number of glass coatings, an optimum processing schedule for the glass-coated alumina system is developed. The results from these studies are then related to the chemical, mechanical, and in-vivo properties of the system as described in later chapters.

Experimental Procedures

The procedure used to form the bioglass-coated alumina system is outlined schematically in Figure 1. Bioglass was prepared from reagent grade sodium carbonate, calcium carbonate, phosphorus pentoxide, and Minusil 5 μm silica.* The composition of the glass is given in Table 1. Premixed batches were melted in platinum crucibles at 1350⁰ C for 4 hours and ground into frit after water quenching. An alumina ball mill and alumina grinding media were used to attain a particle size less than 32 μm (-400 mesh). The fritted bioglass was mixed with 5% (by weight) organic binder,** plus a suitable solvent and the slurry used to coat the

*Pennsylvania Glass Sand Co.

**Acryloid B-7 20% Rohm and Haas Co.

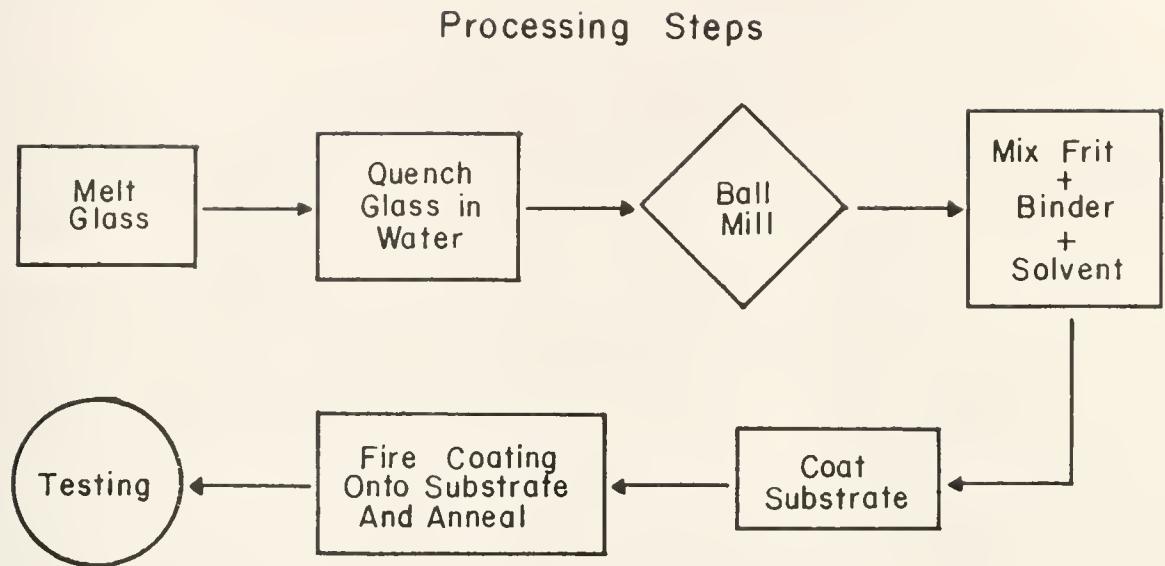


Figure 1. Schematic diagram of processing procedures followed in forming bioglass-coated alumina samples.

alumina substrate by dipping the substrate into the slurry. Upon evaporation of the solvent, a dry, hardened, though delicate, coating of glass frit and binder was formed on the alumina. The composition of alumina* is also given in Table 1.

The coated substrates for initial studies were fired according to the various schedules given in Table 2. In order to prevent thermal shock, the test pieces were heated from room temperature to 1000⁰ C at a rate of approximately 15⁰ C per minute. The samples were immediately transferred to a furnace at the temperatures specified in Table 2 for the corresponding lengths of time. These samples were then placed in an annealing furnace and allowed to cool to room temperature at a rate of approximately 8⁰ C per minute.

Samples were prepared for electron microprobe** (EMP) analysis by polishing cross sections of the glass alumina interface to 600 grit with SiC paper, after which they were polished with a series of diamond pastes ending with a .5 μm grit size paste. The polished test pieces were then coated by vacuum evaporation with 100 $\text{\AA}$ ⁰ of carbon and electrically

*Received from Friedrichsfeld GmbH., Mannheim, Germany.

**Model Ms-64 Acton Laboratories Inc., Acton, Ma.

Table 1

Composition of Bioglass and Alumina Used
(In Wt. %)

Glass	Al ₂ O ₃
45.0% SiO ₂	<.05% Alkali
24.5% Na ₂ O	<.07% Silicate
24.5% CaO	<.03% Iron Oxide
6.0% P ₂ O ₅	.05% Calcia
	1.00% Magnesia
	Balance Alumina

Table 2

Firing Schedule for Preliminary EMP Study

Group 1	1150 ⁰ C - 5 min., 15 min., 30 min., 60 min.
Group 2	1250 ⁰ C - 5 min., 15 min., 30 min., 60 min.
Group 3	1350 ⁰ C - 5 min., 15 min., 30 min., 60 min.

connected to aluminum disks with silver paint. The samples were placed inside the microprobe vacuum chamber on a mechanically driven stage. A 1 μm diameter beam was rastered over a 100 μm distance at a high rate parallel to the glass-alumina interface. This produced a 100 μm^2 area from which x-rays were generated. The beam was then traversed across the interface and data collected every 10-20 μm . Each data point represents the average of three separate counts of 10 seconds each. A constant filament current of 10^{-7} A and a voltage of 20 KV were maintained.

The results of the experiments given in the following section, plus those obtained from in-vitro corrosion data in Chapter III, were used to choose a series of final firing schedules that would produce an optimum coating. These schedules are shown in Table 3. After firing, these samples were prepared for EMP analysis as described above.

Development of a Diffusional Bond in Single-Coated Alumina

The results of EMP studies on diffusion of Al ions into a single glass coating are presented in Figures 2-4. The data are presented as the intensity of Al x-rays as a function of distance into the glass. The dotted line on each graph represents the approximate glass-alumina interface. The intensity of Al x-rays

Table 3
Revised Firing Schedule
For Bioglass-Coated Alumina

<u>First Coat</u>		<u>Second Coat</u>	
<u>Temperature (°C)</u>	<u>Time (min.)</u>	<u>Temperature (°C)</u>	<u>Time (min.)</u>
1350 ⁰	15	----	----
1350 ⁰	15	1150 ⁰	30
1150 ⁰	30	1350 ⁰	15

recorded at each point (when compared to a standard aluminum sample) can be taken as a qualitative measure of the amount of alumina present in the glass coating. In this manner, the graphs represent the amount of Al diffusion into the glass as a function of firing time and temperature. Due to interelement effects, such as matrix absorption and enhancement, and the oxide nature of the system, no attempt to quantify the data further has been made.

The results in Figure 2 clearly show a large change in diffusion of Al into the glass as a function of firing time at 1150°C . For firings of 5 and 15 minutes, the Al has barely diffused halfway into the glass coating. The amount of Al present after 60 minutes of firing time is double that present at 30 minutes. As expected from basic reaction rate theory [33], the diffusion of Al into the glass increases dramatically with time of firing.

The results in Figure 3, for firings at 1250°C , follow the same trend shown in the results of Figure 2. At 1250°C , the diffusion of Al to the surface is very sensitive to changes in the time of firing. The major difference between the firing cycle at 1250°C and 1150°C is that the Al has diffused to the surface of the glass in 15 minutes at 1250°C , which is about twice as far as it had diffused for the same time at 1150°C .

Figure 2. Effect of firing time on the diffusion of Al^{3+} ions into single-coated alumina processed at 1150°C .

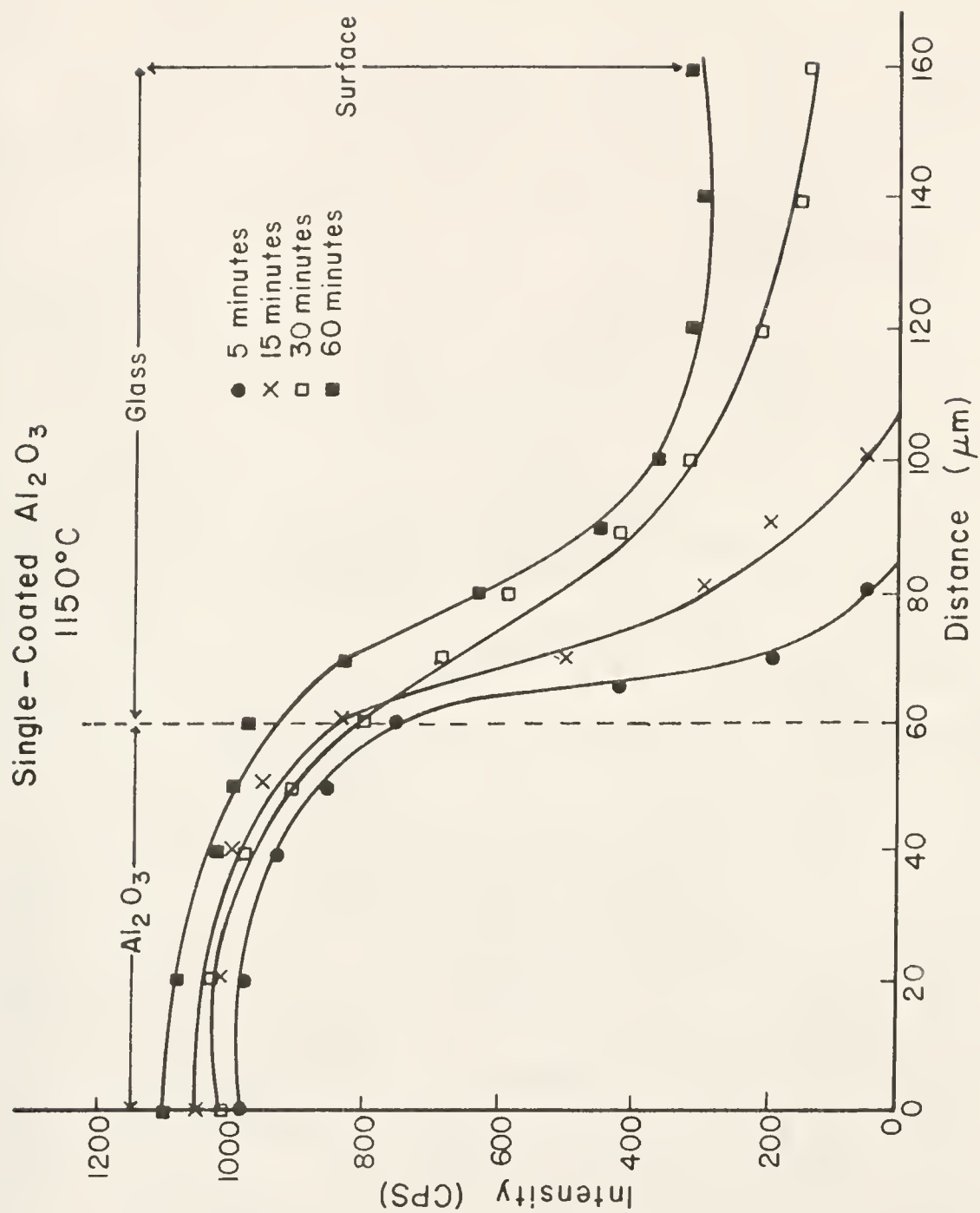
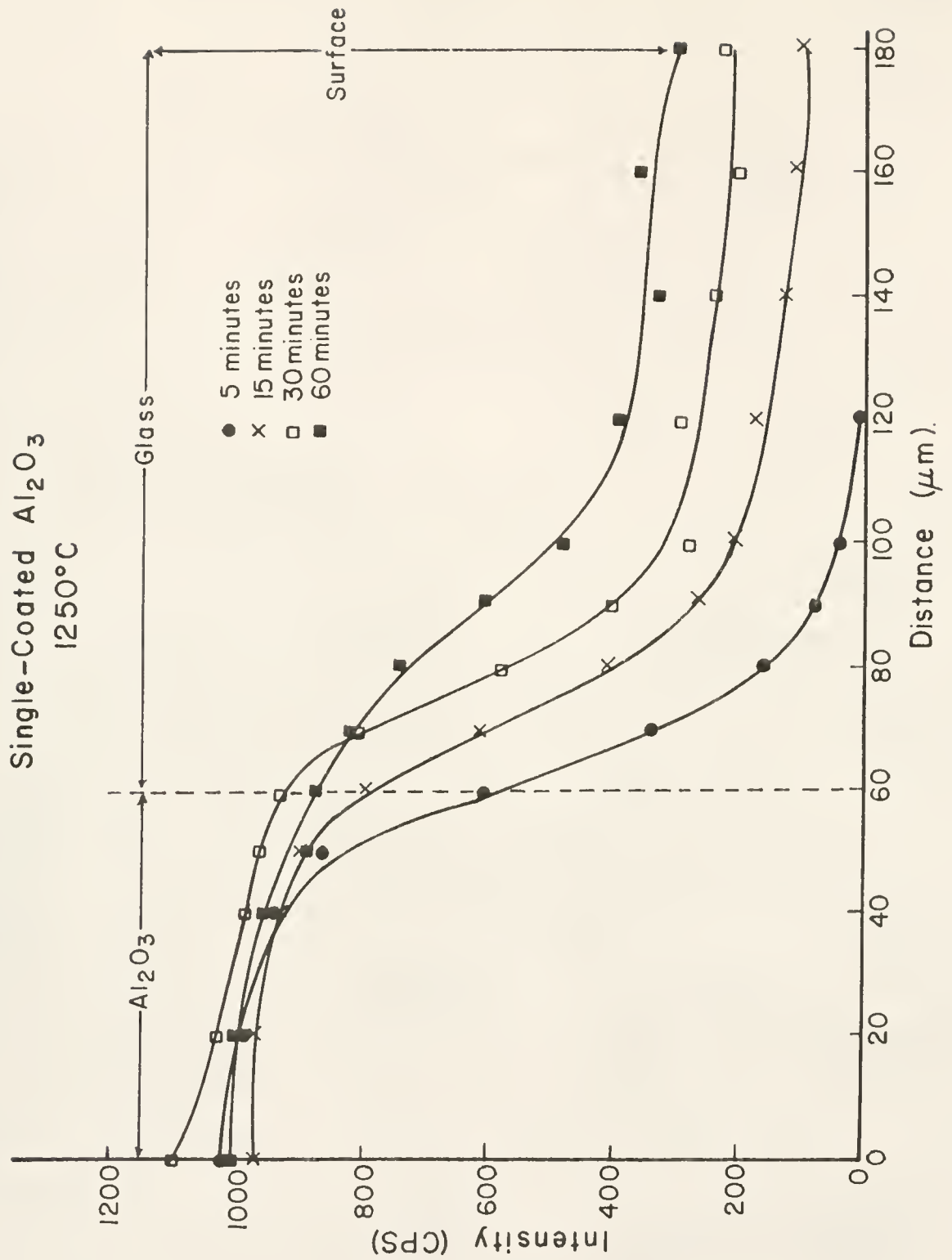


Figure 3. Effect of firing time on the diffusion of Al^{3+} ions into single-coated alumina processed at 1250° C.



In comparison to the two sets of data presented above, Figure 4 shows a much narrower range in the intensity of Al as a function of firing time for 15, 30, and 60 minutes at 1350⁰ C. The total variation in intensity in this range is about 100 cps. It should be recalled that 1350⁰ C is the temperature at which the bulk bioglass is melted and formed. Thus, the low viscosity at this temperature allows for greater diffusion of Al. In addition, if the diffusion of Al into the glass is considered as a thermally activated process, it is clear that as the temperature is increased, the diffusion of Al into the glass will increase. For a firing time of 5 minutes at 1350⁰ C, the diffusion has only proceeded about halfway into the glass coating.

Figures 5 and 6 show the intensity profiles of all five elements present in the system as a function of distance for the specimen fired at 1350⁰ C for 15 minutes. It is interesting to note in Figure 5 that Na has apparently diffused at least 60 μm into the Al₂O₃ substrate. The region marked "interfacial zone" in Figures 5 and 6 was chosen primarily by the intensity drop of Si. This region also contains the steepest slopes of the intensity profiles of the other elements, thus denoting an interfacial bonding region where the composition undergoes large changes.

The results of the microprobe studies shown in Figures 2-4, establish some trends of importance in

Figure 4. Effect of firing time on the diffusion of Al ions into single-coated alumina processed at 1350° C.

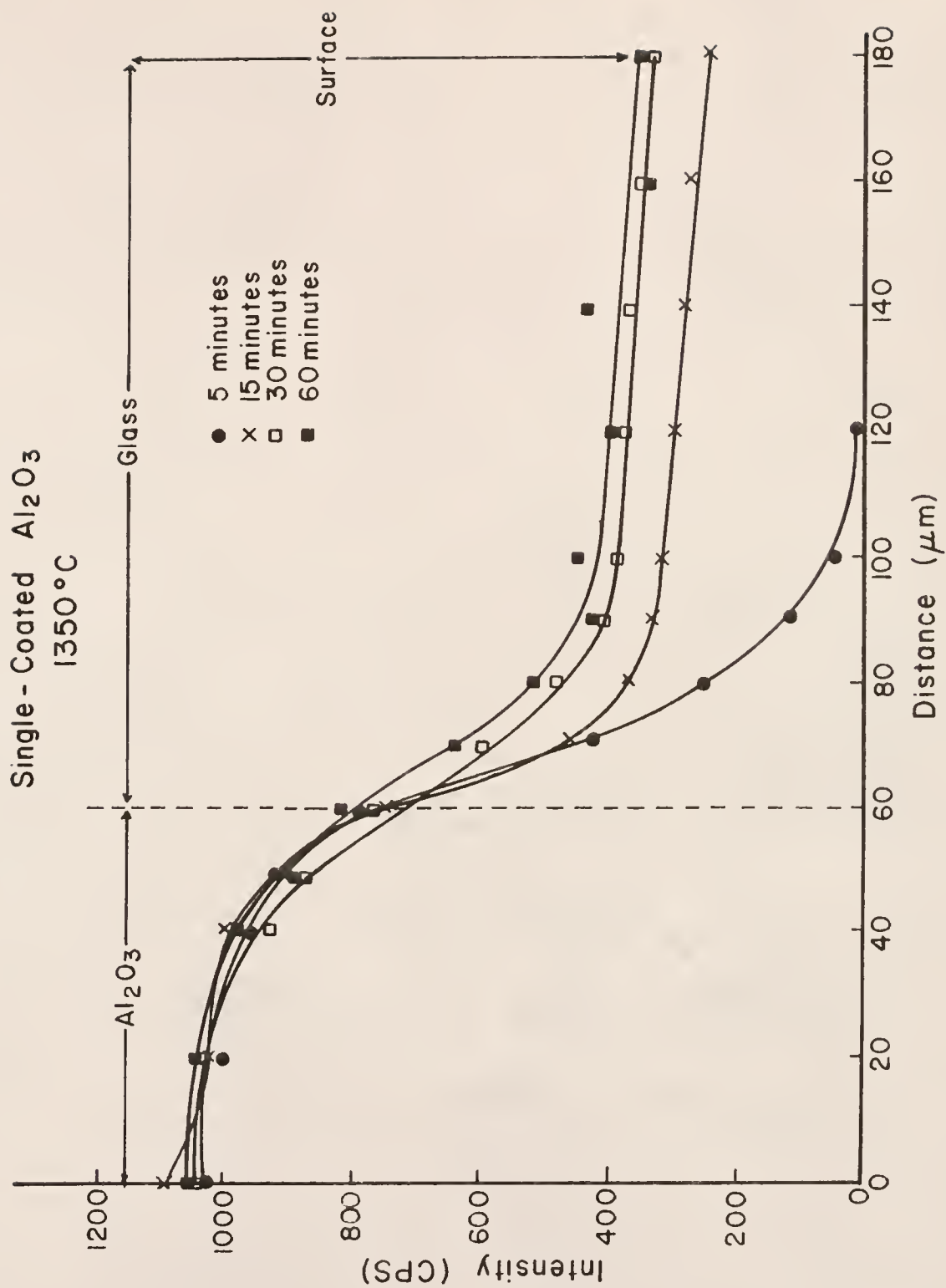


Figure 5. EMP x-ray intensity profiles for Na, Ca, P and Al across the single-coated alumina interface. Specimen processed at 1350° C for 15 minutes.

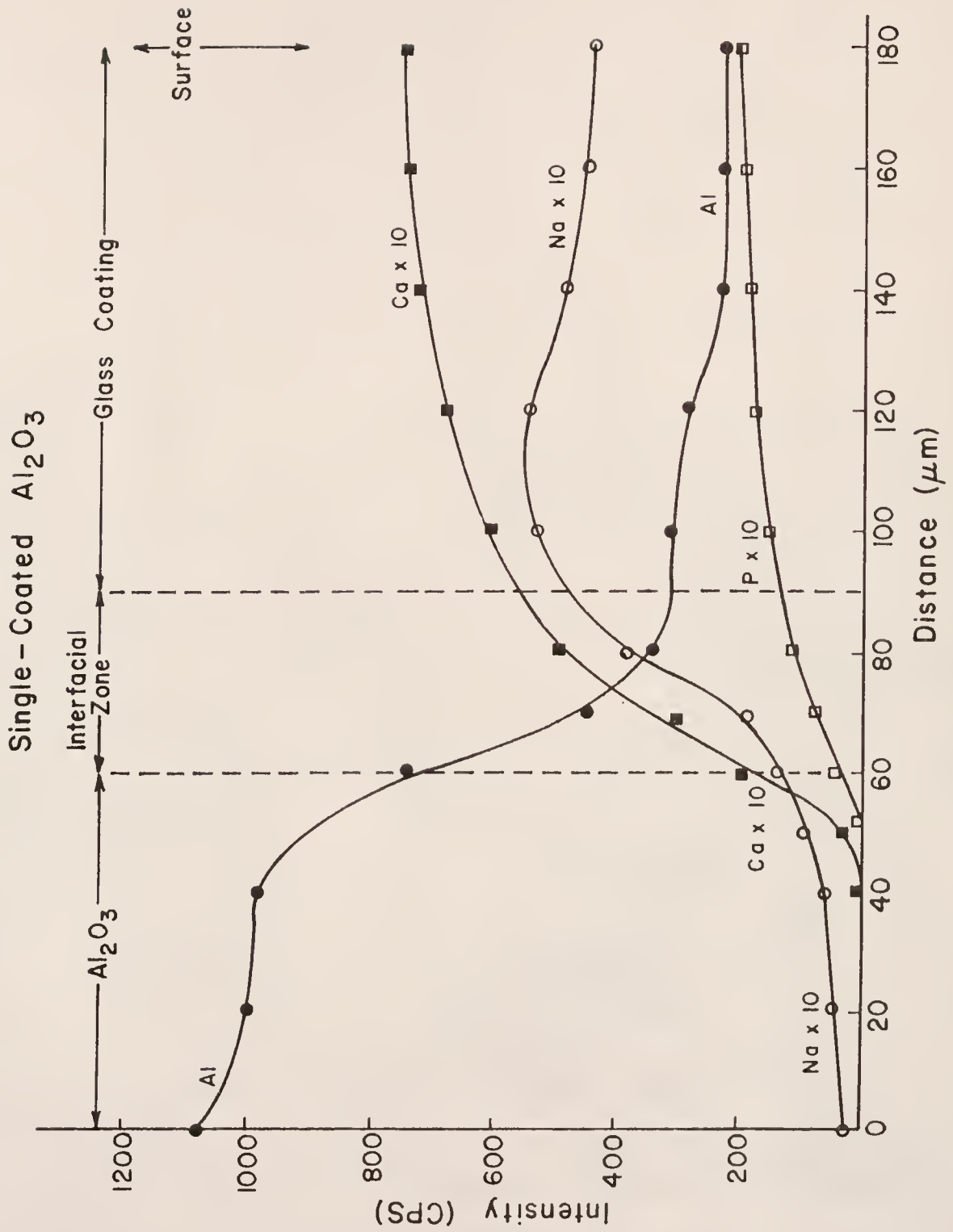
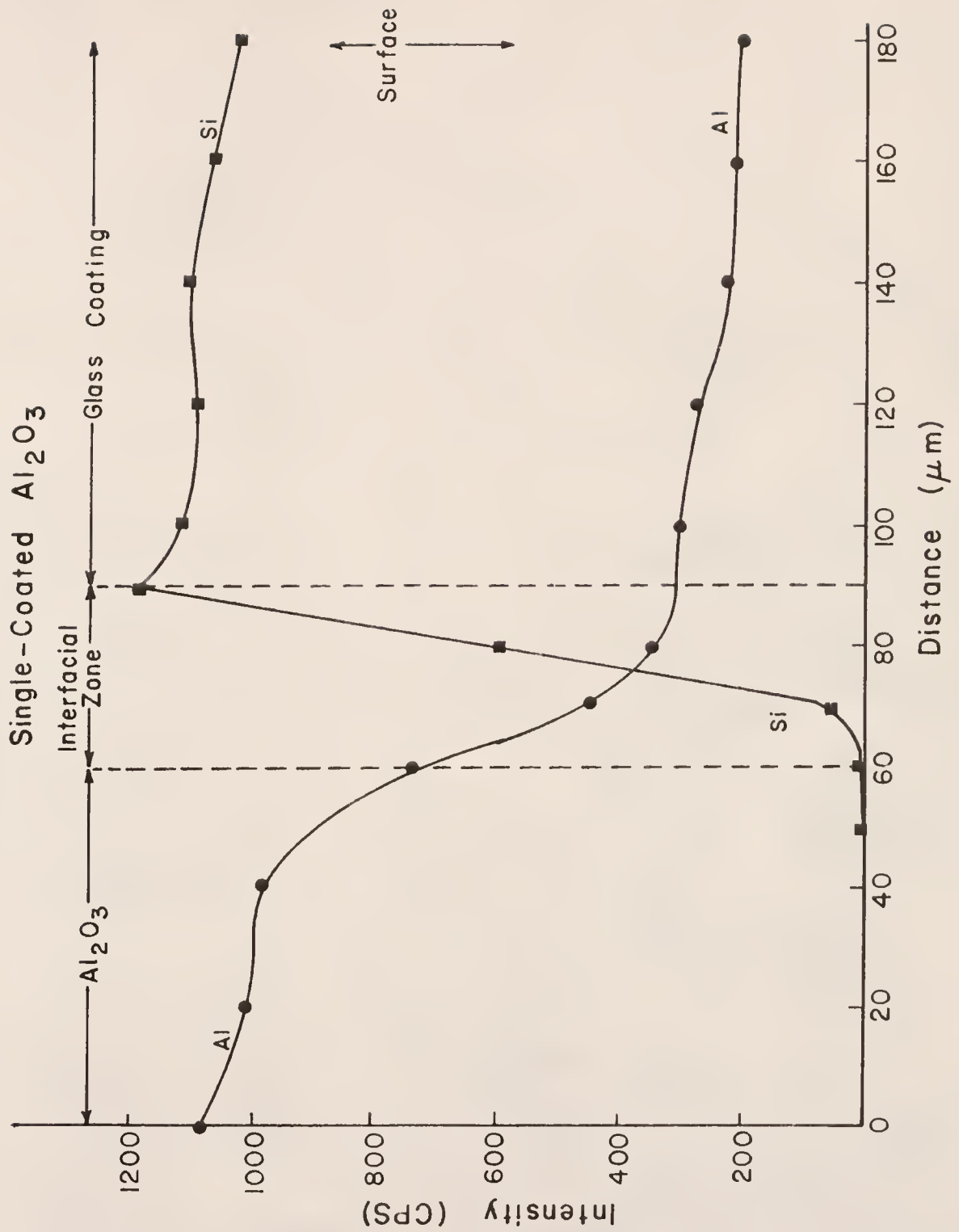


Figure 6. EMP x-ray intensity profiles for Si and Al across the single-coated alumina interface. Specimen processed at 1350 °C for 15 minutes.



understanding the development of the diffusional bond for single-coated Al_2O_3 . First is the fact that either increasing firing temperatures for a given firing time, or longer firing times at a given temperature will give a higher concentration of Al in the glass coating. Secondly, very short times of firing do not allow the development of a good diffusional bond. Optical examination of specimens with short firing cycles (i. e., 5 minutes at 1150°C , 1250°C , or 1350°C) showed rough, irregular surfaces, many of which could be damaged merely by handling. From these facts it is apparent that one condition necessary for development of an adequate diffusional bond is that Al diffuse through most, if not all, of the first layer of the glass coating.

Another important point to consider in the development of the diffusional bond is the wide variation in Al concentration as a function of firing time at 1150°C and 1250°C as compared to 1350°C . From a processing point of view, it would be desirable to minimize the time sensitivity of bond formation, if possible. This strong dependence of diffusion on the time of firing appears minimal at 1350°C . Considering that the bulk bioglass is melted and formed at 1350°C , it is evident that the fluidity of the glass at this temperature allows for easier and more rapid diffusion

of Al into the glass. The narrow range of the diffusion curves at 1350⁰ C supports this point.

Although not shown in graphical form, EMP profiles of the other glass constituents at the various firing times and temperatures showed very uniform and reproducible behavior. In general, there was virtually no Si diffusion into the Al₂O₃ substrate, and the Si intensity profile remained fairly constant. There appeared to be appreciable Ca diffusion into the Al₂O₃ only at 1350⁰ C. The maximum extent of Ca diffusion noted was approximately 30 μ m. However, Na diffusion into the Al₂O₃ substrate was detected to a depth as far as 70 μ m. In comparison, no Na was detected for uncoated Al₂O₃ samples subjected to the same processing procedures.

Microstructure and Characterization of Single-Coated Alumina

From the data presented in Figures 5 and 6, it is evident that considerable diffusion has occurred. The changing intensities of all the elements through the diffusional zone indicate a region of large compositional change. Examination of samples after firing at 1350⁰ C for 15 minutes, revealed a glass layer which was firmly bonded to the alumina substrate. Even upon fracture of the Al₂O₃, the glass layer was adherent to the substrate up to the fracture face. This

fact is demonstrated in Figure 7, which shows such a fracture face. The region between the glass and alumina in Figure 7 is not at all distinct, but rather a diffuse layer, supporting the existence of a diffusional zone. Thus, it seems reasonable that the diffusion process has created a glass of constantly varying composition and, therefore, a constantly changing thermal expansion coefficient. This has allowed the glass to adhere to the substrate even though its initial thermal expansivity ($\sim 140 \times 10^{-7} \text{in./in./}^{\circ}\text{C}$) [37] is much higher than that of the substrate ($50 \times 10^{-7} \text{in./in./}^{\circ}\text{C}$).

Figure 8 is an SEM micrograph of the surface of the sample shown in Figure 7. The most prominent feature of the surface is the crazing, which has resulted in isolated islands of bioglass separated by interconnected cracks. Examination of samples processed under the various firing conditions used in the previous section showed the same phenomenon to varying degrees. An analysis of the average size of the islands of glass was carried out using techniques of quantitative stereology as described by DeHoff and Rhines [38]. Following the procedures described therein, an average size of $166 \text{ }\mu\text{m}$ for the islands of bioglass shown in Figure 8 was obtained. The width of the cracks was found to vary from $0.05 \text{ }\mu\text{m}$ to $1.0 \text{ }\mu\text{m}$. Figure 7 shows one such crack extending from the glass surface to the alumina substrate. This phenomenon was



Figure 7. SEM micrograph of the fracture surface of a single-coated alumina showing bonded region (arrows) between glass (G) and alumina (A), and crack running through glass coating. (1000 x)



Figure 8. SEM micrograph showing the crazed surface of a single-coated alumina. Average size of islands of glass are $166\text{ }\mu\text{m}$ with crack widths ranging from $0.05\text{-}1.0\text{ }\mu\text{m}$.

found repeatedly in examining fracture surfaces of single-coated alumina.

It is a well established fact that a mismatch in thermal expansion coefficients between a glaze and a body can cause stresses that lead to crazing [33, 34]. The stresses in the glaze can be calculated using the following formula:

$$\sigma_{gl} = E(T^1 - T_0)(\alpha_{gl} - \alpha_b)(1 - dj + 6j^2) \quad (1)$$

In this equation, T_0 is the stress-free temperature of the glaze, T^1 is the new temperature reached upon cooling (i. e., room temperature), α_{gl} and α_b are the thermal expansion coefficients of the glaze and body, E is Young's modulus of the glaze, and j is the ratio of glaze to body thickness. If, for the coating under question, T_0 is taken as the annealing temperature of the glass (450°C), the ratio of glaze thickness to body thickness is $j = .033$, and Young's modulus is assumed to be 8×10^6 psi, a stress in the glaze in excess of 82 MPa (12,000 psi) is developed. It is quite clear that this stress exceeds the fracture strength of the bulk bioglass [25], and should be large enough to cause the observed crazing.

Although the above calculations show that crazing might be expected, they do not answer the question of why the crazing occurred in the coatings

even with the diffusion of Al and corresponding changes in composition. In a volume on glass-to-metal seals, Partridge [39] details the use of glasses of graded thermal expansions to provide a seal between a metal and an outer layer of glass of very different thermal expansions. Slight alterations of the expansion coefficients of successive layers of glass by about 5% can create a seal which might otherwise fail. In a similar manner, it was expected that diffusion of Al into the glass coating would create a graded "seal" between the alumina and the outer layer of bioglass.

In an effort to determine the thermal expansion mismatch in the graded glass coatings, the EMP data presented in Figures 5 and 6 were used to obtain new glass compositions at selected points. This was accomplished by assuming that the formation of the diffusional bond was in essence a substitution of Al_2O_3 for a certain percentage of glass. Thus, if the changes in the intensity profiles of Figures 5 and 6 are representative of the system, it should be possible to calculate changes in thermal expansion of the coating as a function of amount of Al_2O_3 present. For example, at a distance of 75 μm , in Figures 5 and 6, the Al intensity has dropped to half its value in the substrate. Furthermore, the intensities of Na, Ca, P, and Si have dropped to approximately half the values obtained from the bulk glass. Following this line of reasoning,

the composition at this point has approximately 50% Al_2O_3 in the glass.

After determining the compositions, the thermal expansions of the new compositions were calculated. Figure 9 is a plot showing the calculated thermal expansion as a function of alumina additions. The data were calculated from an equation given by Takahashi [40] which is based on the dependence of the thermal expansion coefficient on the bond strength between anions and cations in the glass. The equation is given as:

$$\alpha_{\text{tot}} = N_{k1}\alpha_1 + N_{k2}\alpha_2 + N_{k3}\alpha_3 + \dots N_{ki}\alpha_i \quad (2)$$

where N_{ki} is the cation percent of component i and α_i is the thermal expansion of the pure component i . In his equation, Takahashi defines cation percent as the mole percent divided by the number of moles of cations. Thus, 1 mole of Na_2O will have twice the cation percent. Following this equation, the coefficient of expansion for various percentages of Al_2O_3 substituted for bio-glass are presented. It should be noted that the value obtained for bulk bioglass (45S5) by this method agrees very closely with data recently taken at an independent laboratory [37].

Taking the composition midway through the diffusional zone of Figures 5 and 6 at 75 μm as 50% Al - 50% glass, and referring to Figure 9, a thermal expansion

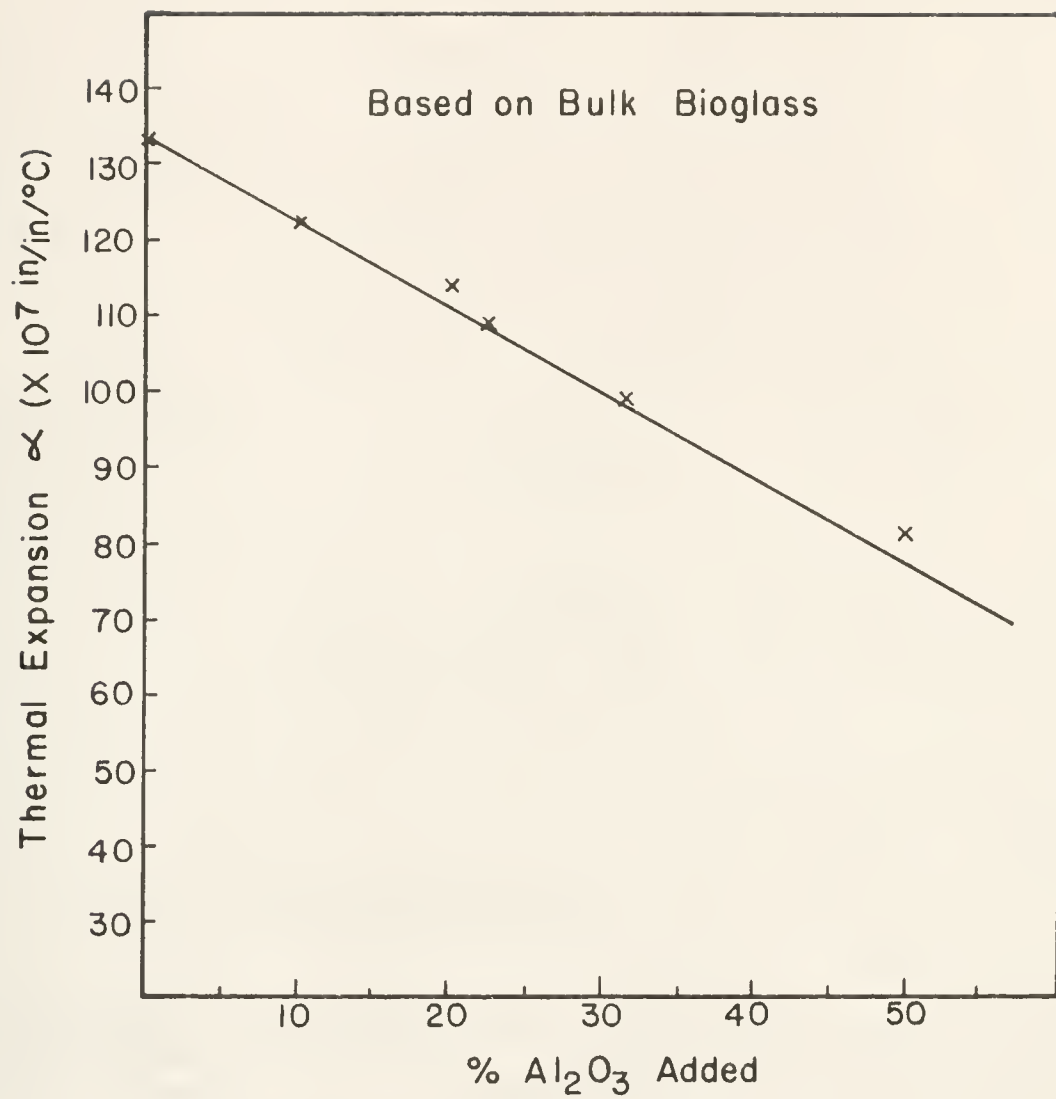


Figure 9. Calculated thermal expansion of 45S5 bioglass as a function of Al_2O_3 additions.

of $80 \times 10^{-7} \text{in./in./}^{\circ}\text{C}$ is obtained. This is compared to an expansion coefficient of $50 \times 10^{-7} \text{in./in./}^{\circ}\text{C}$ for bulk Al_2O_3 . At this point, taking the glaze thickness as $15 \text{ }\mu\text{m}$, and calculating the stress using Equation (1) above, $\sigma_{g1} = 49.7 \text{ MPa (7200 psi)}$. This stress is about equal to the fracture stress of the bulk glass, and should be large enough to cause the observed cracking. The fact that the calculation of the state of stress in the glaze agrees with the observed phenomenon of crazing in the glass coating, supports not only the qualitative results presented in Figures 2-4, but also the calculations of changes in thermal expansion with composition presented in Figure 9.

In addition, a rough guide to minimizing stress due to thermal expansion mismatch in glass-to-metal seals is that the difference in thermal expansion coefficients be less than 10% [39]. It is clear that the expansion difference between the two points shown above is much greater than 10%. Consequently, it should be expected that stresses would develop between the glass coating and alumina in spite of the graded coating.

Double-Coated Alumina

The results given in the two previous sections have demonstrated two important points which must be considered if this system is to be utilized as an

implant material. First is the fact that alumina has been detected at all single-coated surfaces that have given an adequate diffusional bond. Both Weyl and Marboe [41] and Doremus [42] in review papers on glass, have noted that minor additions of Al_2O_3 to a glass may increase the chemical durability by orders of magnitude. As will be shown in later chapters, the aqueous reaction properties of single-coated alumina are greatly affected by the alumina at its surface.

Secondly, the single-coated alumina shows considerable crazing with many of the cracks running through to the substrate. While there has been no evidence that the crazed coating does spall, the possibility of enhanced corrosion within the cracks exists. Enhanced corrosion might lead to accelerated degradation of both the glass coating and the substrate. It is evident that such a possibility must be avoided.

In an effort to eliminate the problems mentioned above, second layers of bioglass were fired onto the first glass coating. The resultant double-coated alumina is shown schematically in Figure 10. An important feature of this system is that the second layer of bioglass is bonded to the first layer of glass. Therefore, thermal expansion mismatch between the glass layers should be minimized, which would eliminate the crazing observed in the single-coated alumina. Because

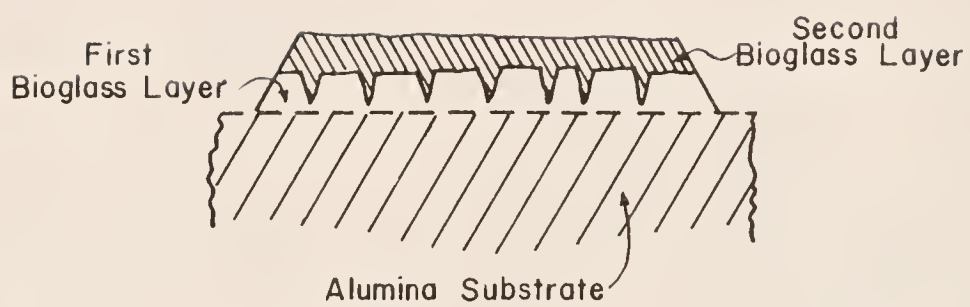


Figure 10. Schematic diagram showing cross section of double-coated alumina.

the bioglass is more reactive than the alumina, an adequate bond between the two glass layers should be achieved at a lower temperature than was necessary for the bonding of the first glass layer to the alumina. This would minimize changes in the surface reactivity of the glass, allowing it to behave more like bulk bioglass.

The firing times and temperatures used for the second coating were the same as those used for the first coating. In order to produce a workable matrix around the second coating variables, only two different first coatings were employed. These were the coatings fired on at 1350⁰ C for 15 minutes and 1250⁰ C for 30 minutes. These were chosen since they both produced adequate coatings. In all cases except the 5 minute firings, a satisfactory second coating was achieved.

Table 4 presents the results of EMP studies conducted to determine if alumina was present at the sample surfaces after double coating. The numbers presented are Al K α x-ray intensities for the double-coated system using a first coating fired at 1350⁰ C for 15 minutes, and 1250⁰ C for 30 minutes, respectively. All data represents the average of five separate measurements. As is to be expected, the increased firing times and temperatures have produced more alumina at the surface of the coated system. From these data,

Table 4

Intensity of CPS of Al Detected at
Sample Surface for Double-Coated Al_2O_3

	Second Coating Temperature		
	1150 ⁰ C	1250 ⁰ C	1350 ⁰ C
	First Coating at 1350 ⁰ C for 15 Minutes		
5 minutes	---	---	---
15 minutes	---	20	50
30 minutes	---	60	105
60 minutes	60	120	200

	First Coating at 1250 ⁰ C for 30 Minutes		
	1150 ⁰ C	1250 ⁰ C	1350 ⁰ C
	First Coating at 1350 ⁰ C for 15 Minutes		
5 minutes	---	---	---
15 minutes	---	30	45
30 minutes	20	50	120
60 minutes	70	160	370

it is evident that the second glass coating should be fired on as rapidly, and at as low a temperature as possible in order to minimize the alumina content in the second coating.

The results of EMP profiling for the sample fired at 1350°C for 15 minutes, then at 1150°C for 30 minutes, are presented in Figures 11 and 12. Comparison of these data with those of Figures 4 and 5 show that the intensity of Al diffused into the second coating has dropped to background levels. This is in agreement with the data presented in Table 4. Note that the level of phosphorus has increased in the second layer of glass as compared to the first layer. It should be pointed out that the second firing of the sample did not alter the diffusional zone much, although the intensity of the Al x-rays detected near the interface has increased somewhat. In later chapters, the increased phosphorus level and decrease in Al will be related to the observed surface reactions of the implant system, both in-vitro and in-vivo.

The surface of the double-coated sample referred to above is shown in Figure 13. The crazing which had been observed in the single-coated system has been reduced practically to zero. In addition, the low firing temperature has prevented the glass from flowing completely, thus resulting in a roughened surface.

Figure 11. EMP x-ray intensity profiles for Na, Ca, P and Al across the double-coated alumina interface. Sample processed at 1350° C for 15 minutes, then at 1150° C for 30 minutes.

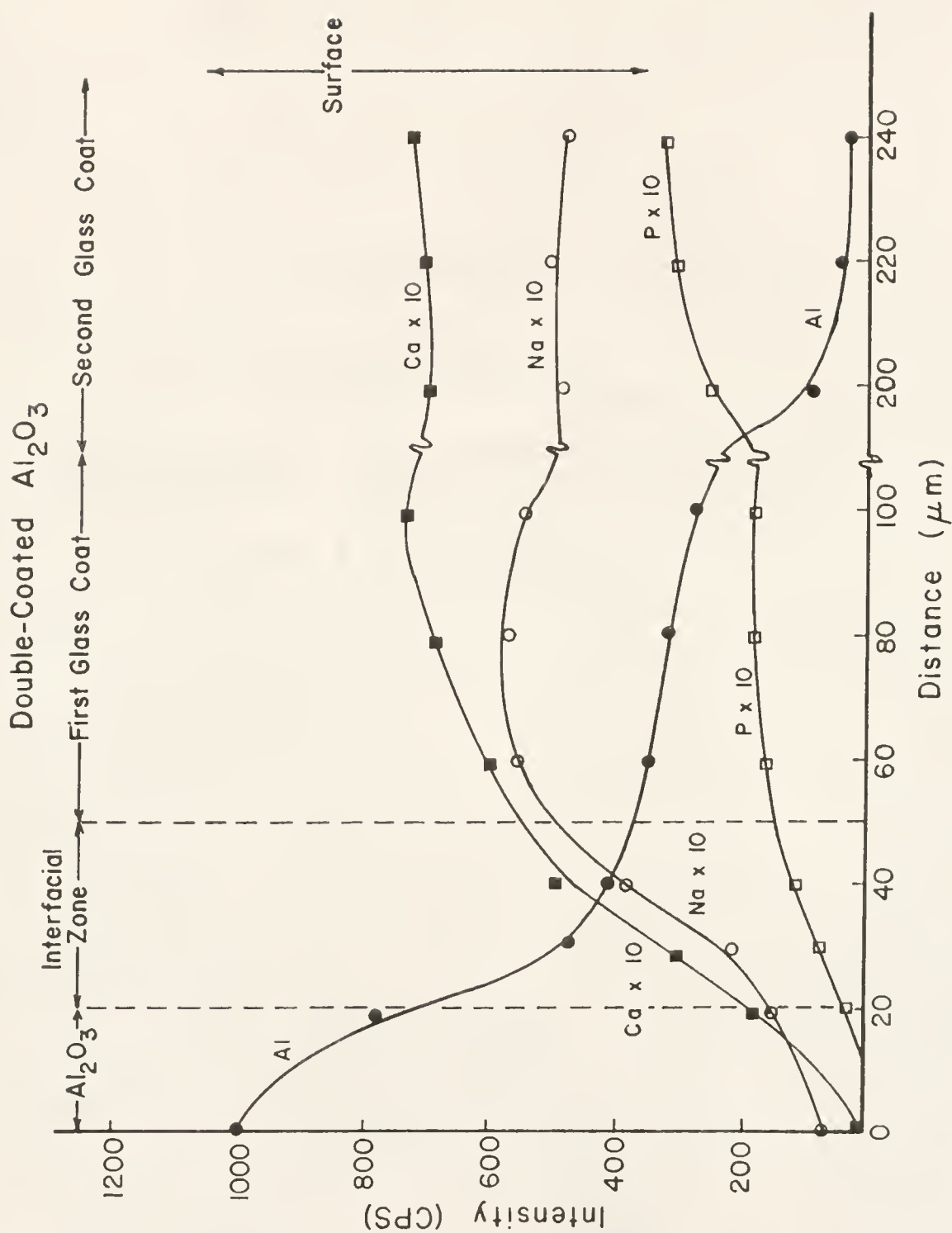


Figure 12. EMP x-ray intensity profiles for Si and Al across the double-coated alumina interface. Sample processed at 1350° C for 15 minutes, then at 1150° C for 30 minutes.

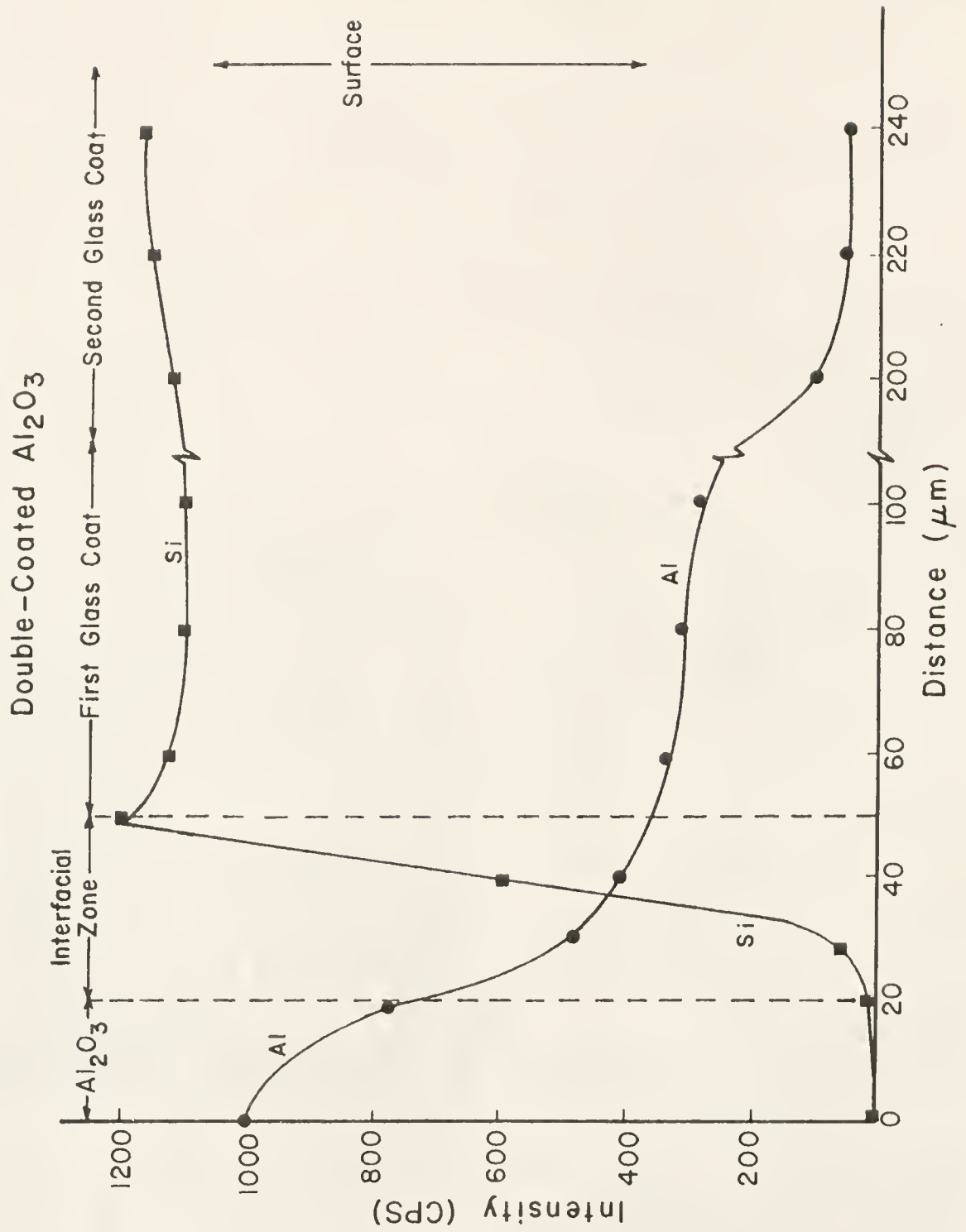




Figure 13. SEM micrograph of double-coated alumina fired at 1350⁰ C for 15 minutes and 1150⁰ C for 30 mintues, showing irregular surface. (1000 x)

Other coatings produced at 1150⁰ C for longer times, and 1250⁰ C for 15 and 30 minutes produced coatings with similar appearances. However, these coatings were found to contain alumina at the surface, a condition which will be shown to be detrimental to the surface chemical properties necessary for a bone-bonding bioglass implant system.

Summary

The development of a diffusional bond between bioglass and high density alumina at high temperatures has been examined. By altering the time and temperature of firing, the extent of diffusion of Al into the glass and Na into the alumina has been varied. The sensitivity of Al diffusion into the glass as a function of firing time has been found to be much greater at 1150⁰ C and 1250⁰ C than at 1350⁰ C. This is due to the fact that the glass has a lower viscosity at this temperature. Very short firing times and low temperatures produced coatings which were not bonded to the alumina surface due to very little diffusion between the materials. Optical examination of the various surfaces showed those produced at 1350⁰ C to be the most uniform and reproducible.

Calculations of thermal expansion changes in the glass coating due to diffusion of Al showed a

decrease in expansion with increasing Al content. These data, coupled with the results of the EMP studies, indicate a graded thermal expansion of the coating, increasing with distance traveled from Al_2O_3 substrate. Calculations of the stresses in the diffusional zone, based on the expansion data mentioned above, showed a stress level high enough to cause crazing (49 MPa). These data were supported by SEM micrographs. Studies of multiple coatings showed that a number of firing schedules could be used to provide a good bond between the glass layers. However, firing the second coating at temperatures over 1150°C for times longer than 30 minutes produce coatings with Al_2O_3 at the surface as shown by EMP analysis. As will be demonstrated in later chapters, this condition must be avoided in order to produce a workable implant system which will bond to bone.

CHAPTER III
IN-VITRO SURFACE REACTIVITY OF
BIOGLASS COATED Al_2O_3

Introduction

The surface chemical behavior of bulk bioglass has been the subject of much study the past few years due to its potential use as an implant material. Of primary importance concerning the surface reactivity of the glass is the type and nature of the reaction film which forms on its surface. It is believed that the reaction film is involved in bonding living bone to the glass [18, 20]. Investigations have shown that small additions of fluorine, boron, and phosphorus alter the surface reactivity of the basic bioglass composition [21, 43]. These additions also affect the biological acceptability of the glass [19]. Furthermore, mechanisms of the reaction processes of various bioglass compositions have been studied in order to determine those factors which are essential in controlling the bonding of the glasses to living bone [43, 22, 23]. From these studies, a number of conditions necessary to promote bone-bonding have been enumerated. Perhaps the most important of these is that the glass be able to form a stable calcium phosphate layer [19-22, 43].

In light of the information available from the surface reaction studies of bioglass, it is apparent that before bioglass-coated alumina can be considered an acceptable bioactive implant system, its surface reactivity must be fully understood. It is the purpose of this study to employ techniques already established in previous works [22, 23, 43-46] in order to determine the surface reactivity of the glass-coated alumina system. These techniques include infrared reflection spectroscopy (IRRS), ion concentration analysis of corrosion solutions, scanning electron microscopy (SEM) with energy dispersive x-ray analysis (EDXA), and Auger electron spectroscopy (AES). By understanding and monitoring the surface reactivity of the coated system, it is possible to relate processing variables to such behavior. By systematically altering the processing variables, a range of surface reactivities can be effected.

Experimental Procedures

Samples for in-vitro experiments were prepared according to the firing schedules presented in Chapter II, Tables 2 and 3. The surfaces were left as fired. The prepared samples were then immersed in aqueous buffered solutions at a pH of 7.2 and a temperature of 37° C. Buffering was accomplished with trishydroxymethyl

aminomethane or succinate buffer [47]. The tris buffer was prepared from solutions of .2 M tris aminomethane and .2 M HCl, and mixed with deionized water to produce the proper pH. The succinate buffer was prepared from solutions of .2 M sodium succinate and .2 M HCl, and mixed with deionized water to obtain a pH of 5.4 at 37° C. All samples were maintained under static conditions. A Coleman Metrion IV pH meter was used to monitor changes in pH (accuracy ± 0.05). Duration of exposure of the samples to the buffered solutions ranged from 0.1 hour to 2500 hours.

Upon removal from solution, each sample was dried and subjected to infrared reflection analysis. The spectra were measured from 1400 cm^{-1} ($7.25\text{ }\mu\text{m}$) to 250 cm^{-1} ($40\text{ }\mu\text{m}$), for both reacted and unreacted specimens. All measurements were made with a Perkin-Elmer 467 Grating Infrared Spectrophotometer equipped with a specular reflectance accessory.

Ion concentration analyses of the reaction solutions were performed using both atomic emission spectroscopy and colorimetry. Atomic emission spectra were measured for sodium and calcium, and ionic concentrations determined by comparison with known premixed standards which were analyzed at the same time as the unknown solutions. Colorimetric determinations of silica and phosphate were carried out using a Hach Direct Reading Colorimeter. This method relates the intensity

of a specific wavelength of light passing through the sample to the concentration of that particular ion.

Samples were prepared for the SEM by drying in air after removal from solution and connecting the piece to an aluminum disc with silver conductive paint. After drying the paint, samples were coated with $\sim 100 \text{ \AA}$ of carbon. A Cambridge Scanning Electron Microscope equipped with an Ortec Energy Dispersive X-Ray Analysis System, and a JEOL 35 Scanning Electron Microscope with a KEVEX energy dispersive x-ray system were used for this investigation.

Samples for AES analysis were exposed to solution and placed in a stainless steel vacuum chamber maintained at a back pressure of 1×10^{-7} Torr. To minimize damage to any corrosion film which formed, a very low beam current was used ($\sim 5 \text{ \mu a}$). Beam energy was maintained at 2 KV for the experiments. The angle of incidence of the electron beam was maintained at a 45° angle to prevent unstable charging of the specimen surface. The specimen stage was then cooled to cryogenic temperatures and maintained at 110° K to facilitate the detection of sodium under the electron beam. Chemical profiles were obtained by the concurrent use of ion milling and AES. An argon beam of 2 KV was used to remove the outermost atomic layers of the samples.

Results and Discussion

In-Vitro Reactivity

Figures 14 and 15 show the results of exposing bioglass and various glass-coated aluminas to buffered aqueous environments. Previous studies [19] have established a correlation between the rate of pH change of buffered solutions exposed to implant materials and the histologic response of the material in hard tissue. The time required to override the pH of a buffered solution has been shown to be a measure of the reactivity of the sample surface. This is due to the change in pH of the solution being a result of an alkali ion-proton exchange between the glass and the solution [48]. Thus, it is clear that the various firing schedules employed to produce the glass-coated alumina have yielded a wide range of surface reactivity. Furthermore, the data indicate that the reactivity of the double-coated alumina most closely resembles that of the bulk bioglass.

The time dependent behavior of ion release into solution is presented in Figures 16-19 for the the bulk bioglass and single and double-coated alumina. These data reveal the wide range of reactivity shown in the data of pH and ion concentration vs. time. The single-coated alumina samples show as much as an order of

Figure 14. Effect of various firing schedules on the time required to override the pH in succinate buffer at 370 C.

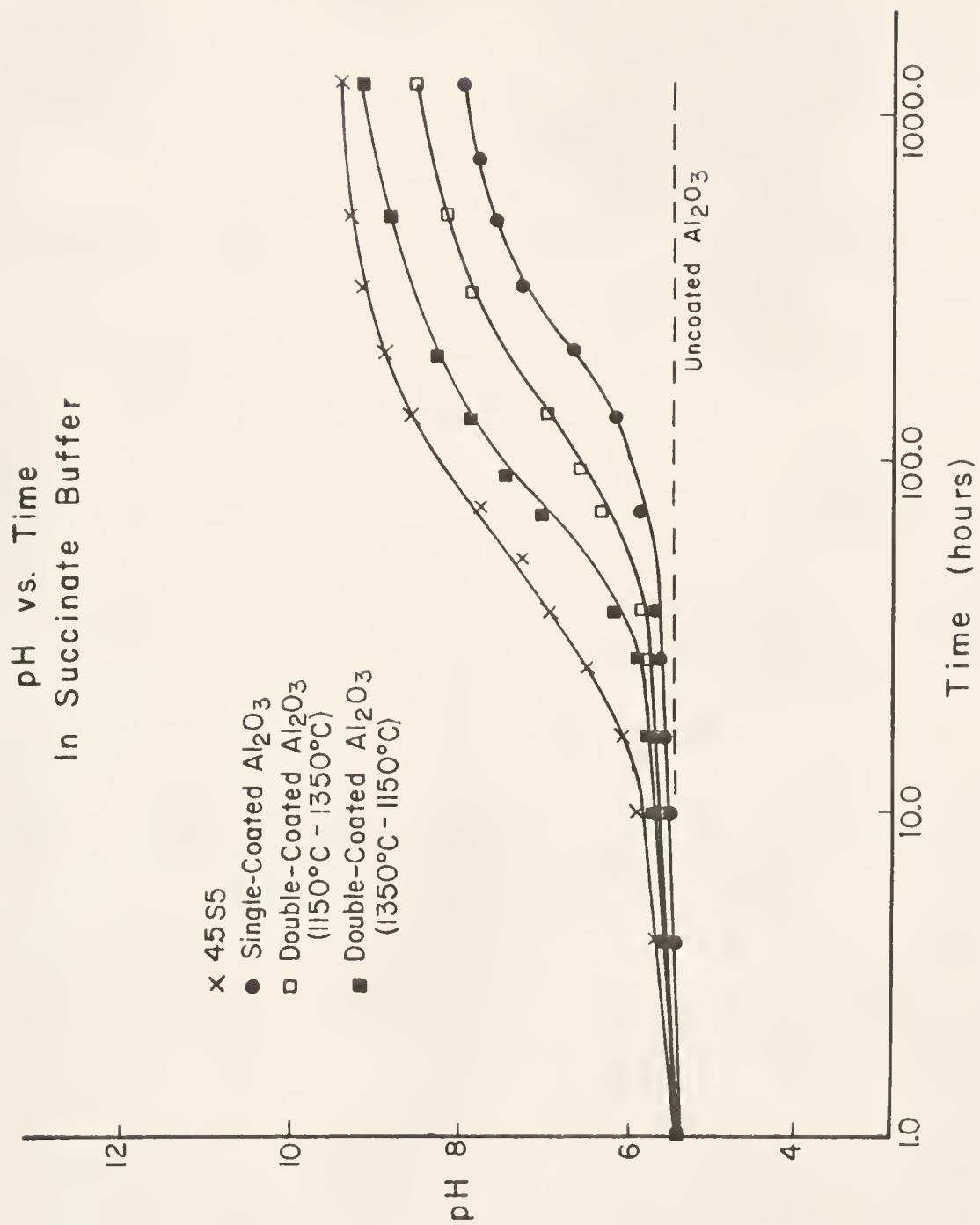
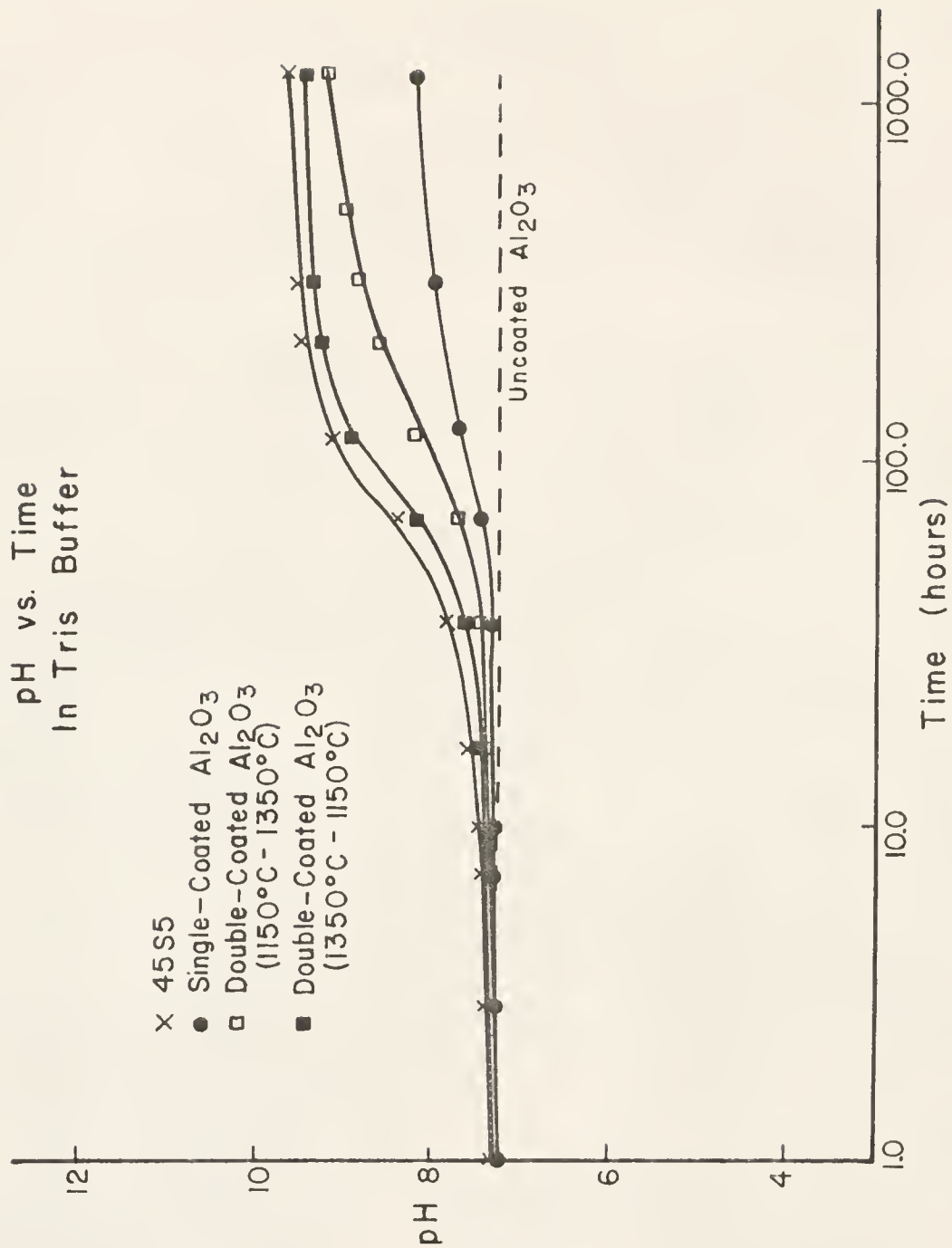


Figure 15. Effect of various firing schedules on the time required to override the pH in tris buffer at 37° C.



magnitude less reactivity than the double-coated alumina under the same solution conditions. Moreover, the release of phosphorus into solution for the single-coated alumina (shown in Figure 16) is quite different than that for either double-coated alumina or bulk glass. In describing the reaction behavior of the bulk glass in-vitro, Clark [21] points to the decrease of phosphorus in solution after 10 hours as a precipitation onto the glass surface which is related to the formation of the calcium phosphate layer. The absence of such a reaction is an indication that the single-coated alumina system might not be suitable as a bone-bonding material.

In comparing the rate of ion release of the double-coated alumina to the bulk glass, two important points must be brought forth. The first is that the rate of sodium release into solution is slightly higher for the double-coated alumina than for the bulk glass during the very early stages of reaction, as shown in Figure 17. Weyl and Marboe [41] have presented the results of Keppeler's study of increased sodium at a glass surface. In this work, heat treatments of glass rods up to 575° C for up to 7 hours, reveal the formation of a surface layer of high alkali content relative to the untreated glass. (Weyl and Marboe believe this increased alkali diffusion is caused by surface tension of the outer layer of glass.) These results show that it is probable that the processing of the bioglass-coated alumina (see Chapter II) has

Figure 16. Time dependent release of P from various coated alumina surfaces at 37° C.

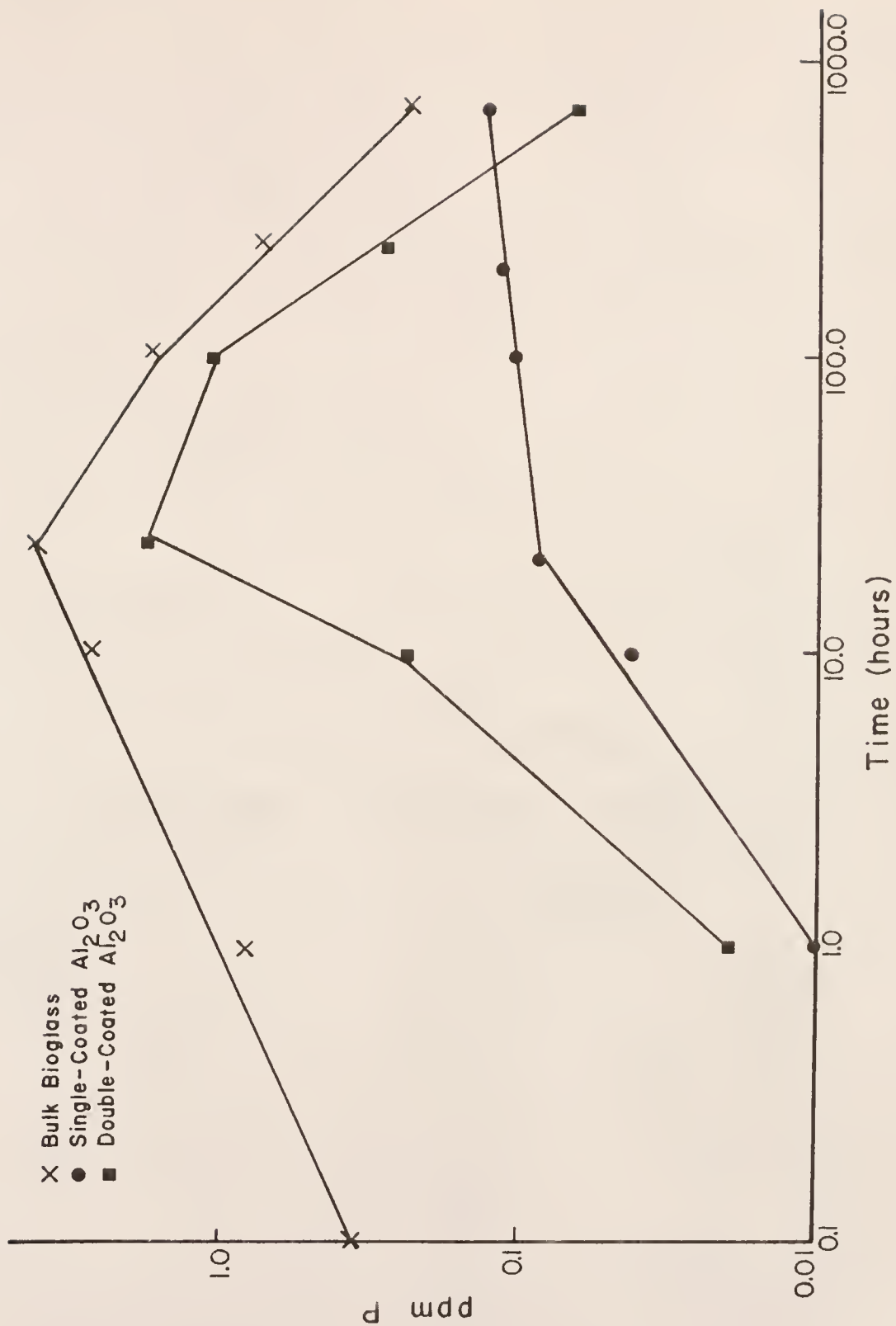


Figure 17. Time dependent release of Na from various coated alumina surfaces at 37° C.

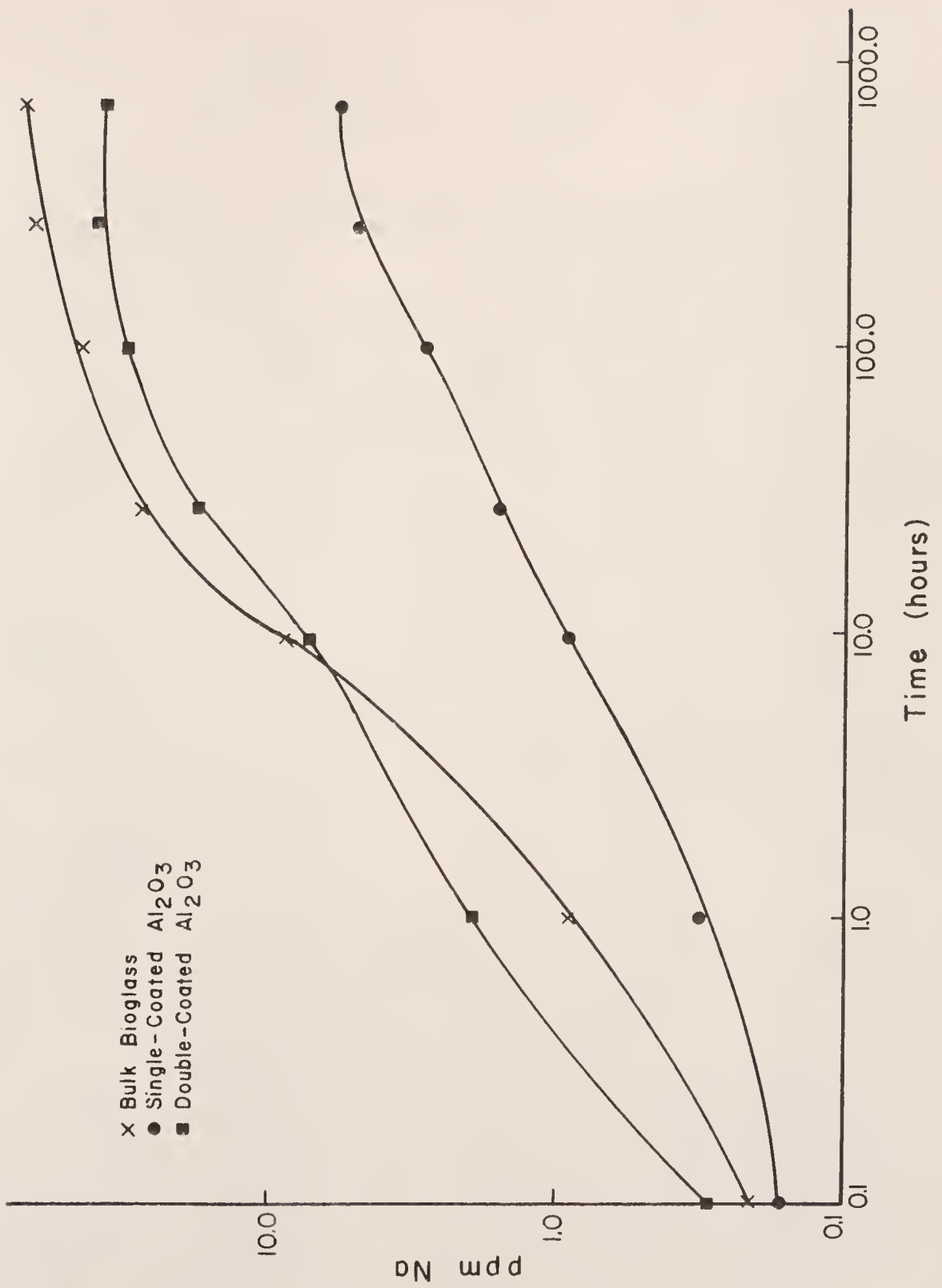


Figure 18. Time dependent release of Ca from various coated alumina surfaces at 37° C.

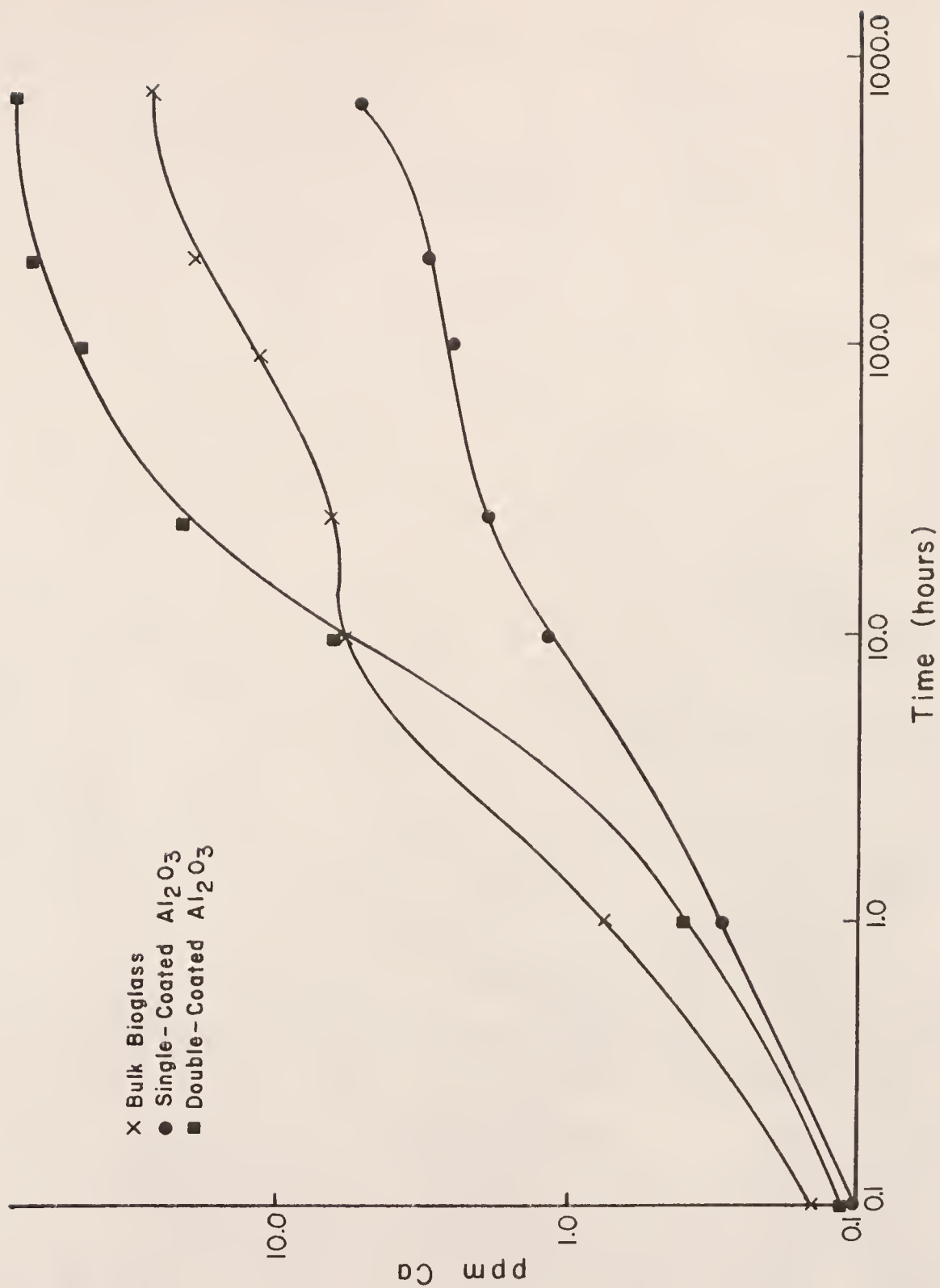
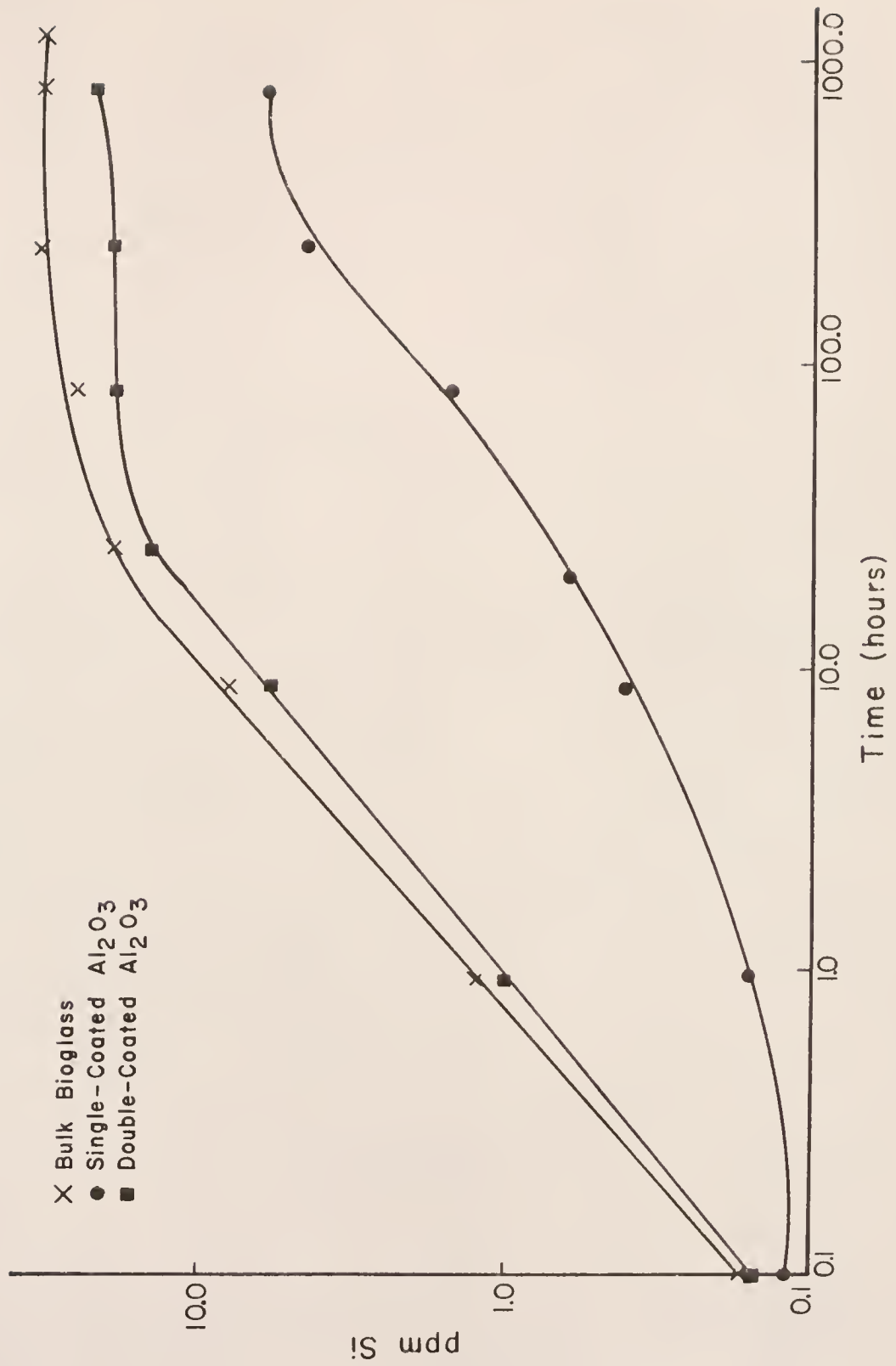


Figure 19. Time dependent release of Si from various coated alumina surfaces at 37° C.



contributed to an initially higher surface alkali content than that found in bulk bioglass.

The second point to be made is that the release of phosphorus into solution by the double-coated alumina system follows the same pattern as that of the bulk glass. Although the total amount of phosphorus released into solution is less for the coated system than for the bulk, the decrease in phosphorus in solution shows a precipitation occurring in the coated system. At the same time as the phosphorus is precipitating out of solution, release of the other ions into solution is being retarded. This change in the rate of ion release, even before the solution has reached $\text{pH} = 9$, denotes the formation of some protective film. As pointed out by Clark [21], the formation of a calcium phosphate film significantly influences the surface reactivity of bulk bioglass. By isolating the bulk glass from the aqueous environment, the calcium phosphate film decreases the rate of surface attack.

To further analyze the film formation postulated from the data presented above, an SEM investigation was performed. Figures 20 and 21 are scanning electron micrographs of double-coated alumina surfaces, as prepared and after 10 days reaction in tris buffer. The surface in Figure 20 is an as-cast surface. The rough appearance of the surface is due to an incomplete melting of the glass frit at the processing temperature.



Figure 20. SEM micrograph of unreacted double-coated alumina. (200 x)



Figure 21. SEM micrograph of double-coated alumina after 10 day reaction in tris buffer. (5000 x)

Figure 21 clearly shows the existence of a reaction film on the surface. X-ray spectra taken from double-coated alumina both before and after solution reaction are shown in Figure 22. Both spectra were taken at a magnification of 20,000 x, under identical beam conditions of 20 KV and 140 μ a of beam current. The total number of x-rays counted in each spectrum were approximately the same (192,360 for the spectrum of Figure 20 vs. 198,647 for Figure 21). Maintaining these conditions permits a qualitative comparison of the x-ray data collected. These results show that after 10 days in solution, a film rich in phosphorus and calcium has formed on the glass-coated alumina surface. In addition, the sodium peak has completely disappeared. This fact is in agreement with the findings of Clark [21] and Pantano [24] that the reaction of bioglass in tris buffer proceeds by a rapid dealcalization of the surface. The data presented in Figure 22 compare favorably with SEM-EDX data of bulk bioglass presented by Clark [21]. A much higher phosphorus content is detected by EDX analysis after 1 day and 10 days of reaction for the bulk glass. The same condition holds true for the coated alumina sample after 10 days of reaction.

Examination of the x-ray spectrum from the unreacted sample shows the presence of aluminum. This result was not expected as EMP studies conducted on the

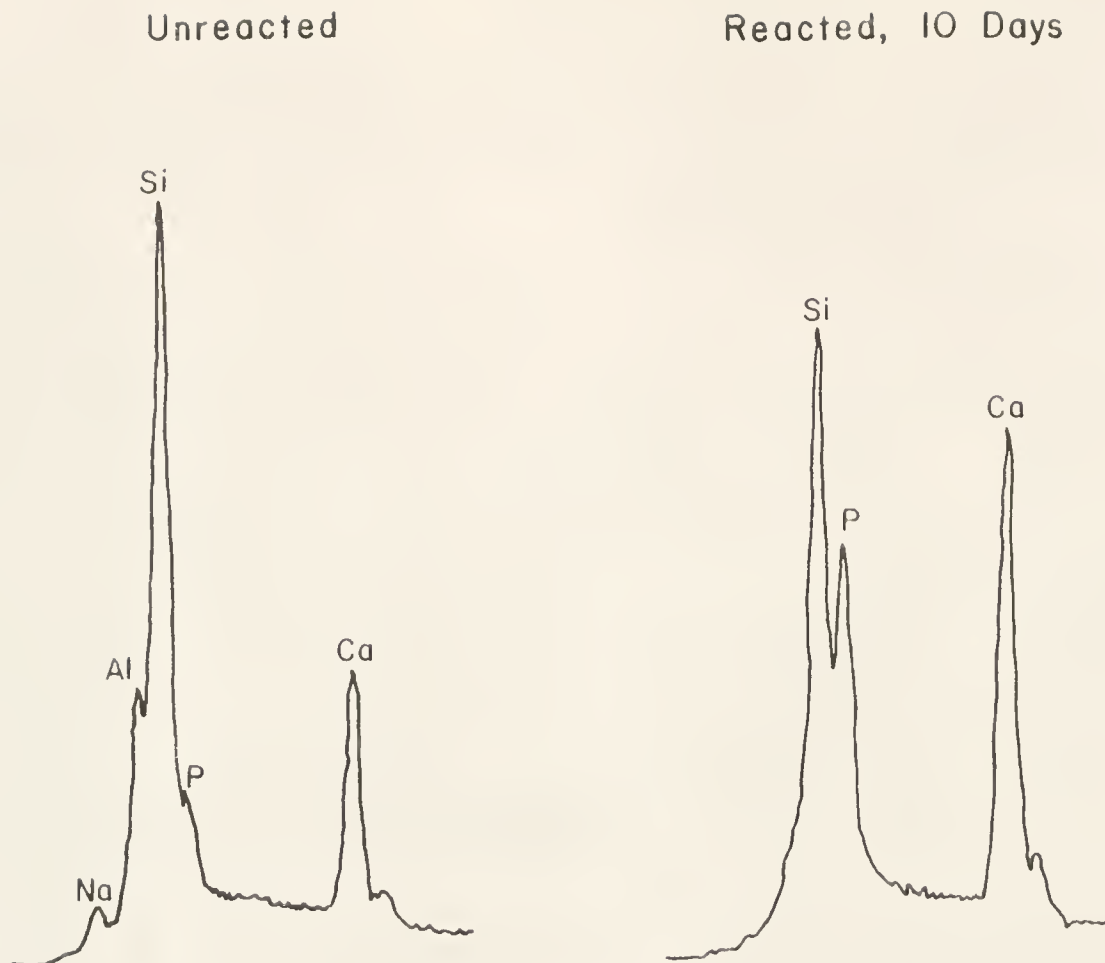


Figure 22. EDX analyses taken from double-coated alumina before reaction in tris buffer and after 10 days reaction in tris buffer.

double-coated alumina system did not detect the presence of aluminum anywhere near the surface of the glass coating (see Chapter II). To check that aluminum was, in fact, present at or near the entire surface, and not merely a contaminant in one localized area, x-ray spectra were taken from 10 different areas on the sample. By way of comparison, 10 areas were counted on both single-coated alumina and bulk glass. Beam conditions were held constant, and each x-ray spectrum collected consisted of approximately 200,000 total counts. Table 5 presents the results of these experiments as ratios of number of counts of the particular element to the number of total counts. These data show the presence of Al in the double-coated sample. While the results presented here are not quantitatively precise and cannot be directly related to the percentage of the particular element in the sample, they clearly show differences in the composition of the various materials. It is interesting to note that the ratio of Ca to total counts is highest for the double-coated alumina. Referring back to Figure 18, the amount of calcium leached into solution is greatest for the double-coated system. Comparison of the x-ray data with Figure 19 shows a strong correlation between the amount of Si detected with EDX and the amount of Si leached into solution. It should be noted that the sampling depth of the x-ray data from the SEM is on the order of 1 to 2 μm .

Table 5

EDX Analysis of Various Processed Surfaces

	$\frac{\text{Na}}{\text{T.C.}}$	$\frac{\text{Al}}{\text{T.C.}}$	$\frac{\text{Si}}{\text{T.C.}}$	$\frac{\text{P}}{\text{T.C.}}$	$\frac{\text{Ca}}{\text{T.C.}}$
Single-Coated Al_2O_3	.04	.32	.20	--	.42
Double-Coated Al_2O_3	.05	.03	.32	.01	.60
Bulk Bioglass	.07	--	.38	--	.54

T.C. = Total Counts

Figure 23 presents IRRS data comparing the various surfaces listed in Table 5. Sanders, et al. [49] have shown that both chemical and structural changes occurring in soda-lime-silica glass can be detected by IRRS. This technique has been applied by Clark [21] while investigating bulk bioglass. The reflectance peak of bulk bioglass at 1035 cm^{-1} has been shown by Clark [21] to be due to one of the Si-O-Si stretch vibrations. The peak at 910 cm^{-1} in the bulk glass has been shown to be due to a silicon nonbridging oxygen peak. The results for the single-coated Al_2O_3 presented in Figure 23 show that both the silicon-oxygen stretch vibration and the silicon nonbridging oxygen peak have been shifted to lower frequencies. In studies conducted on soda-lime-silica glass, Clark [50] has shown that by increasing alkali content up to 22% Na_2O for a constant amount of CaO , a shift in the frequency of the Si-O stretch maxima to lower wave numbers will occur. He also points out that even small additions of Al_2O_3 and CaO to a glass will cause a coupling of the Si-O stretch vibration with the modifier, thereby shifting the maxima to lower wave numbers. Thus, the large shift observed in the Si-O stretch maxima in the single-coated Al_2O_3 is due to the large amount of Al_2O_3 present. The shift in the Si-O stretch maxima of the double-coated Al_2O_3 from 1035 cm^{-1} is much less drastic, but still quite substantial and reproducible. Comparison

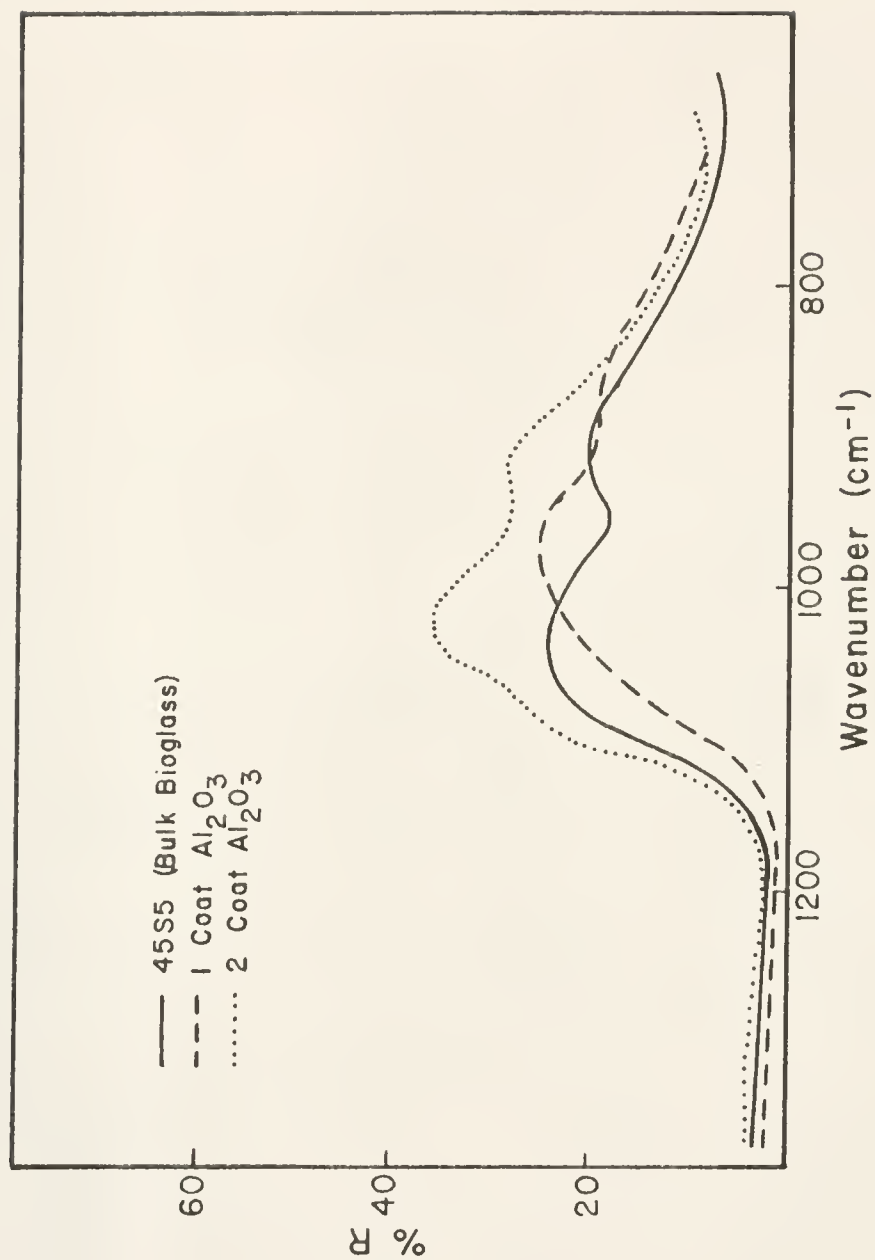


Figure 23. Infrared reflection spectrum for single and double-coated alumina and 45S5 bulk bioglass.

of the x-ray data in Table 5 shows an increase in both Ca and Al in the double-coated Al_2O_3 over the bulk glass. Consequently, it is not clear whether the shift in the peak is due to the Al_2O_3 or CaO which has been detected by x-ray.

In order to determine the location of the Al with respect to the surface of the glass, AES was employed in conjunction with ion-milling. Auger chemical profiles of both single and double-coated Al_2O_3 are shown in Figures 24 and 25. The ion milling rate for various glasses has been calculated by Pantano [24] to be approximately $30 \text{ \AA}/\text{min}$. Therefore, these chemical profiles are sampling to a depth of about $.2 \text{ }\mu\text{m}$. While the spectrum in Figure 11 shows a considerable amount of Al present in the single-coated sample, no Al was detected in the double-coated material. A comparison of the raw data in Figure 25 with data from bulk bioglass [21] show a higher Ca level in the coated sample than in bulk glass. There also appears to be somewhat less Si in the coated sample than in the bulk glass. Thus, an enrichment of the unreacted surface of double-coated bioglass in Ca coupled with less Si at the surface has caused the IRRS spectra to shift to lower frequencies. The x-ray data from SEM-EDXA presented in Table 5 support this point.

Figure 24. AES chemical profile for unreacted single-coated alumina.

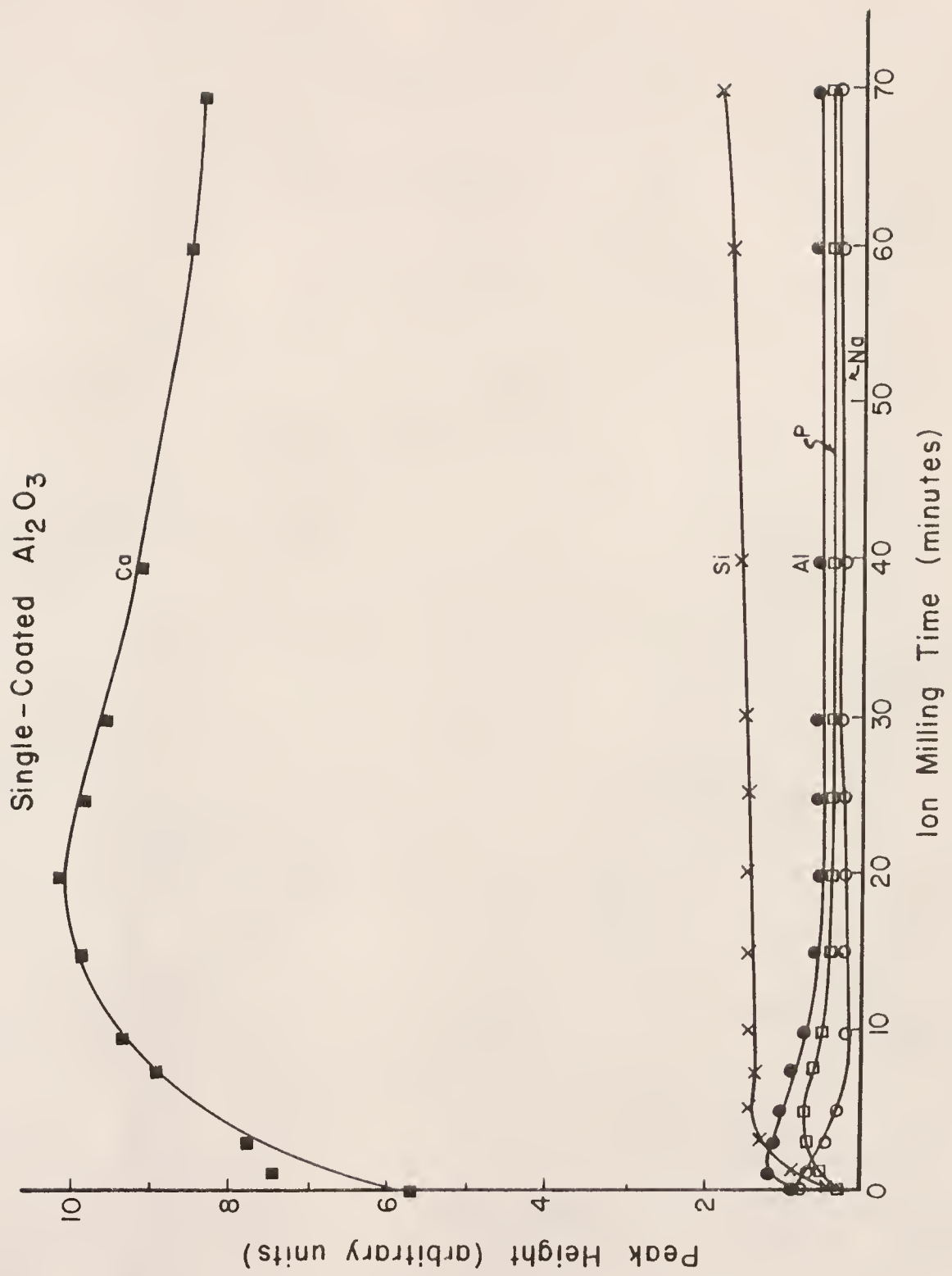
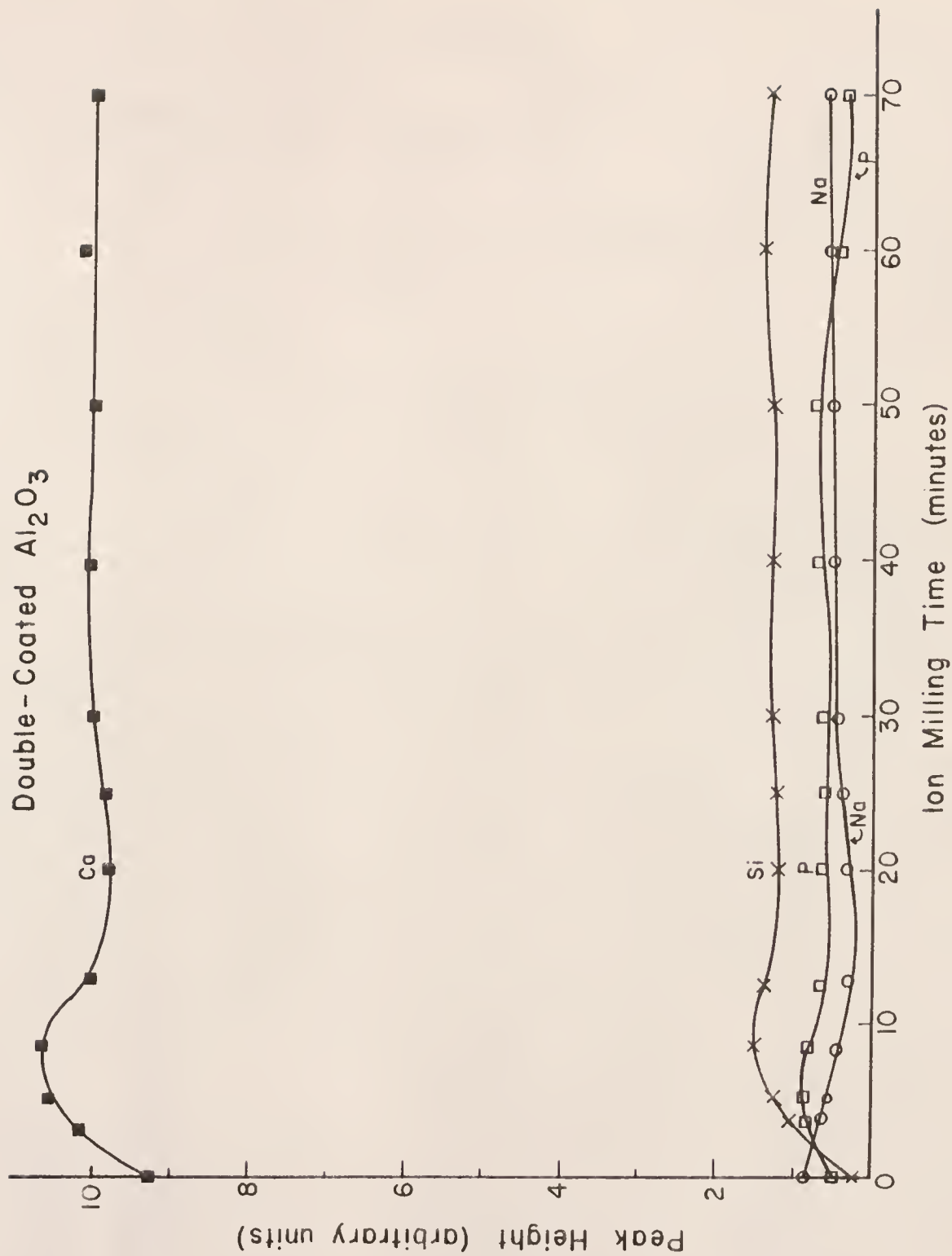


Figure 25. AES chemical profile for unreacted double-coated alumina.



Effect of Al on Reaction Film Formation

The previous section has shown that a wide range of reactivities for the coated alumina system are possible by varying the processing conditions. The fact that the double-coated system will form a calcium-phosphate rich film in-vitro has also been demonstrated. However, the presence of alumina in the glass coating was, for the double-coated alumina, an unexpected result. In addition, the reaction behavior of the double-coated alumina has not duplicated that of the 45S5 composition. It has previously been demonstrated that crystallization of bioglass does not affect its bone-bonding characteristics [17, 51]. These studies have also shown that crystallization has not affected the in-vitro corrosion behavior. Therefore, it seems likely that the presence of alumina has in some way altered the surface reactivity of the coated alumina system. The implications of this alteration will be discussed further in Chapter V. This section will attempt to explain the observed differences in the in-vitro surface reactivity between the coated alumina and 45S5 bioglass.

Figure 26 is an AES chemical profile of the double-coated alumina system after 1 day reaction in tris buffer. This profile shows a very thin calcium phosphate rich surface layer, followed by a layer which is somewhat enriched in silica. There is also

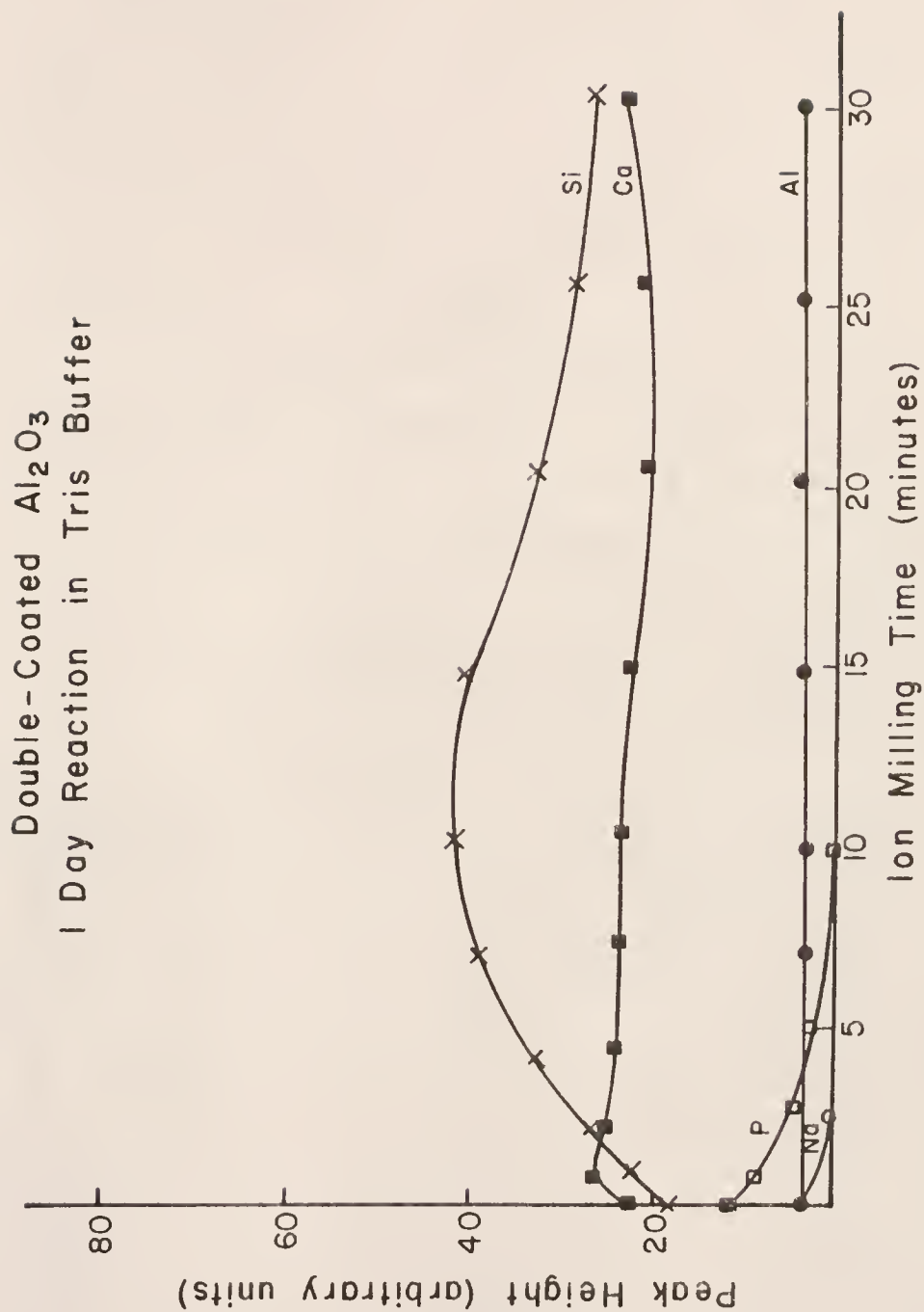


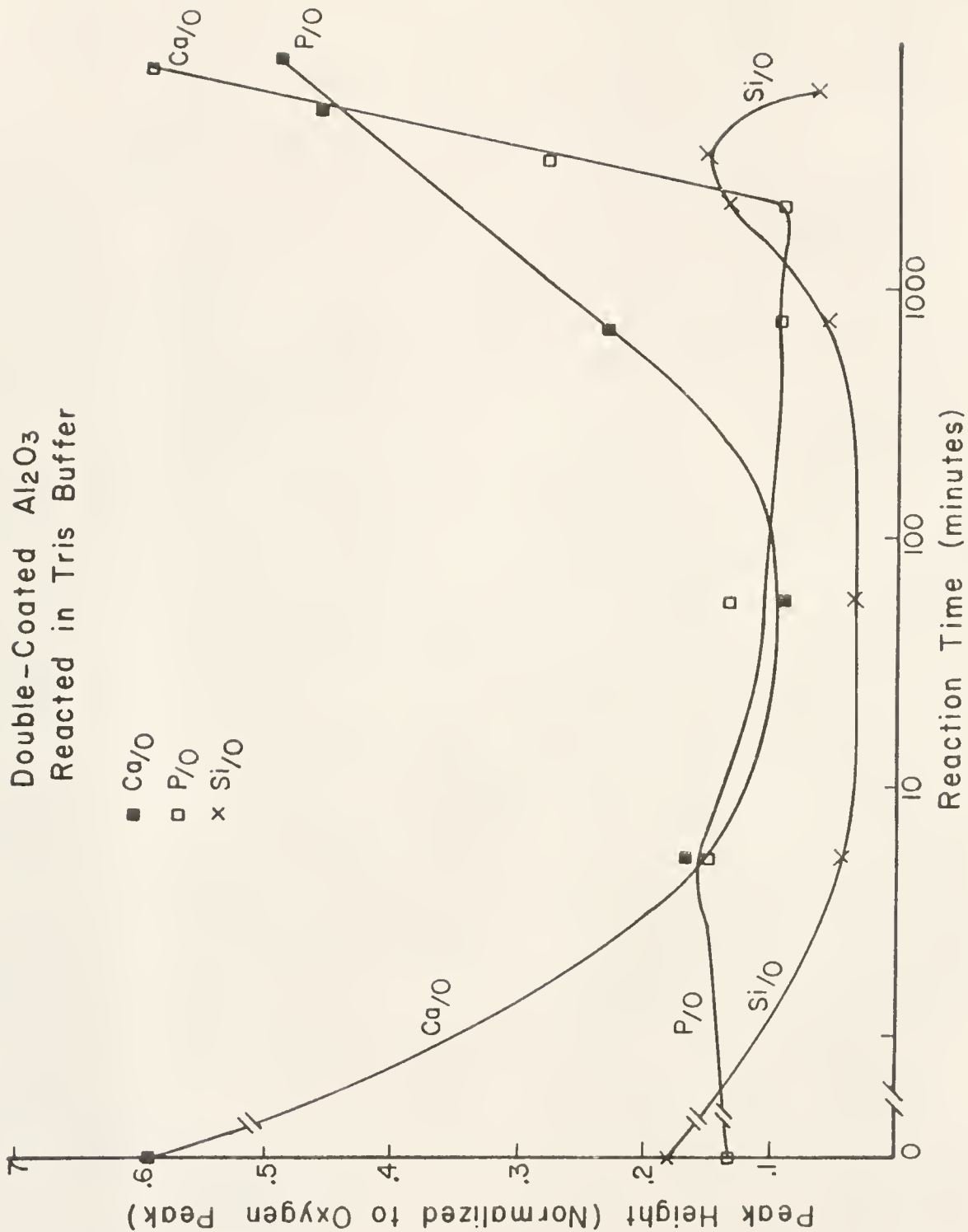
Figure 26. AES chemical profile for double-coated alumina after 1 day reaction in tris buffer.

some Al present throughout the profile. By way of comparison, Pantano [22, 24] has shown 45S5 bioglass to possess a surface film rich in calcium and phosphorus after only one hour in tris buffer. The calcium phosphorus film described by Pantano contains much less silica than is present in the double-coated alumina. In addition, the silica-rich gel layer immediately beneath the calcium phosphate film has been shown to be 3-4 μm thick for the bulk glass. It is clear from Figure 26 that only a slight enrichment of silica has occurred for the coated sample, and that only after a day of exposure.

Figure 27 monitors the development of the calcium phosphate film of the double-coated alumina as a function of reaction time. The peak heights are normalized to that of oxygen for plotting convenience. The large initial decrease in calcium is consistent with the ion release data presented in the previous section. However, the build-up of a calcium phosphate rich film is not in evidence until some 3000 minutes of reaction time (2-3 days). This is much slower than the rate of formation found by Pantano [24] for bulk 45S5 bioglass.

Figure 28 is an IRRS curve of double-coated alumina after 3 days in tris buffer. It is compared to a spectrum of the 45S5 bioglass reacted in tris buffer for 10 hours. The formation of the double peak at 560 cm^{-1} and the peak at 1045 cm^{-1} has been shown by

Figure 27. Change in surface composition of double-coated alumina as a function of reaction time in tris buffer at 37° C.



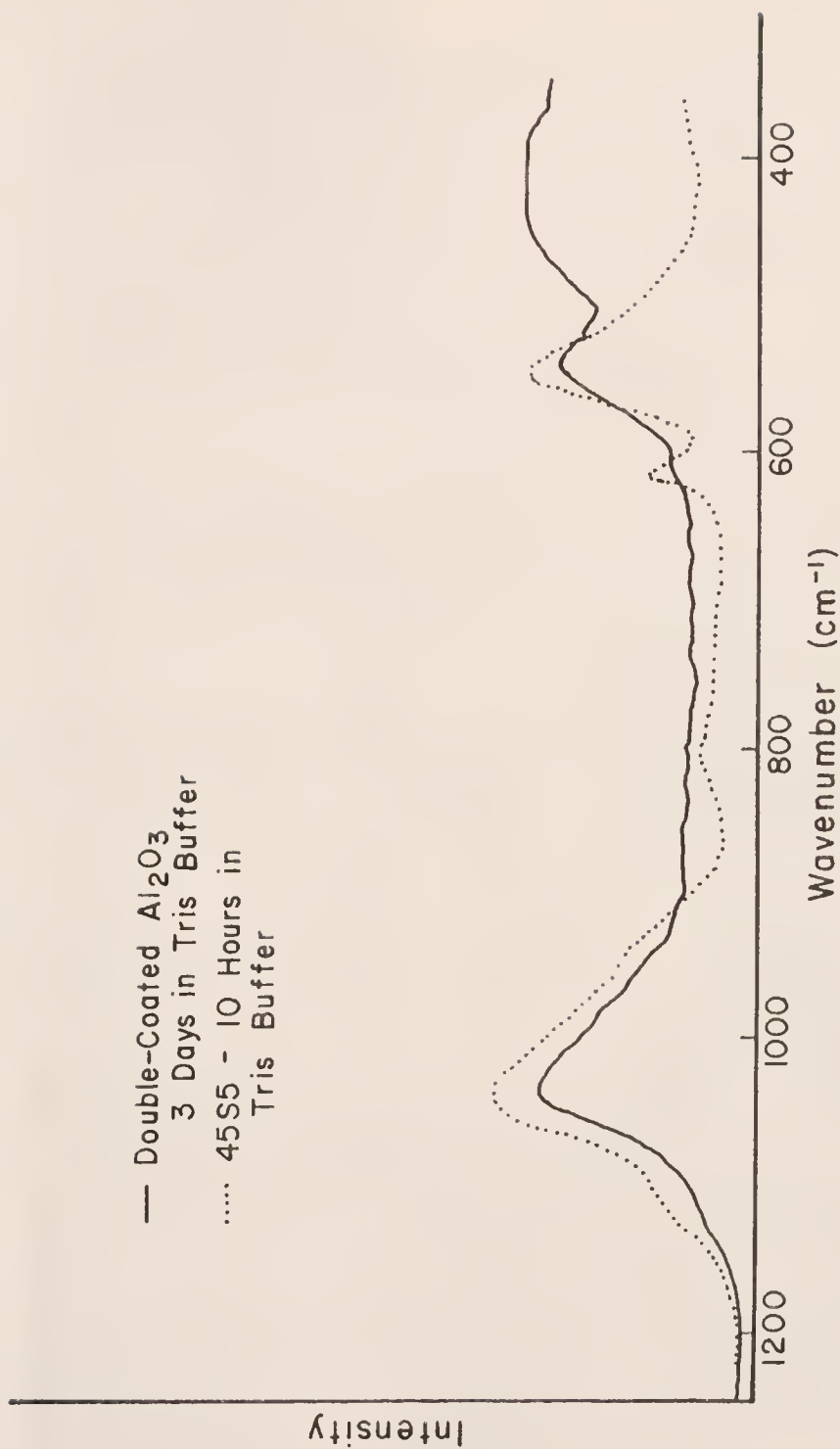


Figure 28. Infrared reflection spectrum of double-coated alumina after 3 days reaction in tris buffer and 45S5 bioglass after 10 hours reaction in tris buffer.

Clark [21] to be associated with an apatite structure, most likely a form of hydroxyapatite. Comparison of the two curves reveals that the double-coated alumina does, in fact, have calcium phosphate rich surface layer. In addition, the broad peak in the spectrum of the double-coated alumina at 450 cm^{-1} is associated with a Si-O-Si rocking vibration. As the IR spectrum samples a depth of approximately $.5\text{ }\mu\text{m}$, the Si-O-Si peak could be due to a very thin calcium phosphate layer. However, inspection of Figure 27 demonstrates the presence of Si at the sample surface after 3 days. In light of this information, combined with the appearance of the film as shown in Figure 21, it is more likely that the calcium phosphate film is nonuniform.

The differences in film formation between the double-coated alumina and bulk bioglass mentioned above could be due to either the alumina present in the coating, or to some other changes due to processing, such as concentration gradients or surface films. To determine the role of alumina in film formation, a batch of 45S5 bioglass with 5% Al_2O_3 was prepared following procedures used in preparation of standard bioglass samples. Reagent grade chemicals were used. The batch was melted in a Pt crucible at 1350°C for 24 hours, and annealed for 6 hours at 475°C . All samples used for analysis were ground to a 600 grit finish.

Figure 28 is an IRRS spectra comparing the 45S5 glass and the double-coated alumina. The shift of the Si-O-Si stretch vibration from 1035 cm^{-1} to 1020 cm^{-1} is to be expected due to the coupling of Al with the Si-O-Si vibration [50]. Attempts to monitor the corrosion behavior of the 45S5 + 5% Al_2O_3 glass with IRRS proved unsuccessful due to a rapid roughening of the surface. It is interesting to note that after 1 day and 3 days in tris buffer, no spectrum was obtained for this glass. In comparison, the double-coated alumina showed a spectrum after 3 days in tris buffer very much like that of bioglass after 10 hours.

To determine exactly what type of film had formed on the surface of the new composition with Al_2O_3 present, an Auger spectroscopic analysis was performed. Figures 29 and 30 compare the Al_2O_3 containing glass before reaction and after 1 day in tris buffer. It is apparent that all the phosphorus and sodium which had been detected before surface reaction has been leached from the glass. This has left a silica rich surface. The leaching of alkali from the alumina-containing glass proceeds in the same manner as in the 45S5 composition. However, after 1 day corrosion, the alumina-containing glass still has a silica rich layer. Auger data of the surface of the alumina-containing glass after 3 day corrosion in tris buffer also shows

Figure 29. AES chemical profile for unreacted 45S5 + 5% Al_2O_3 bioglass.

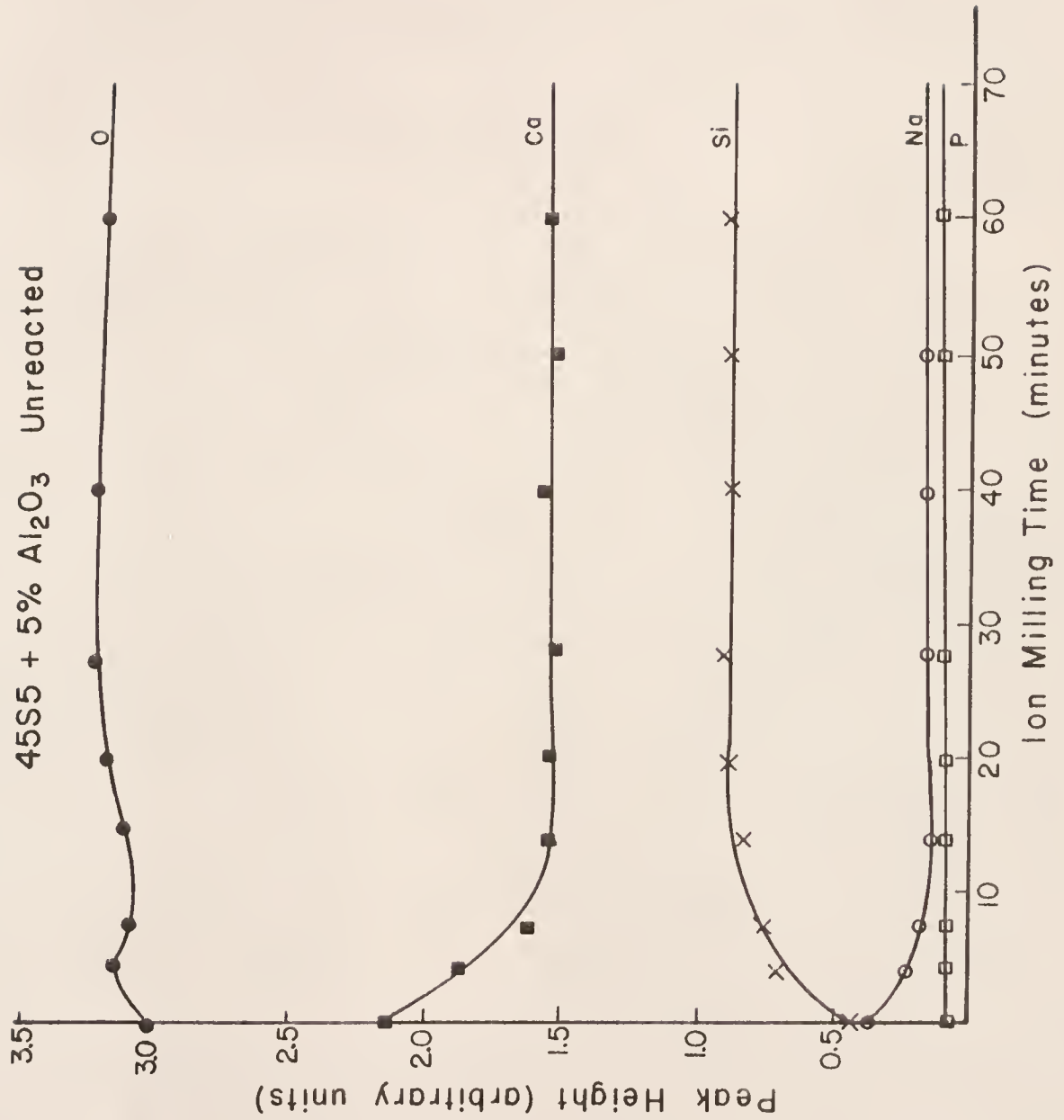
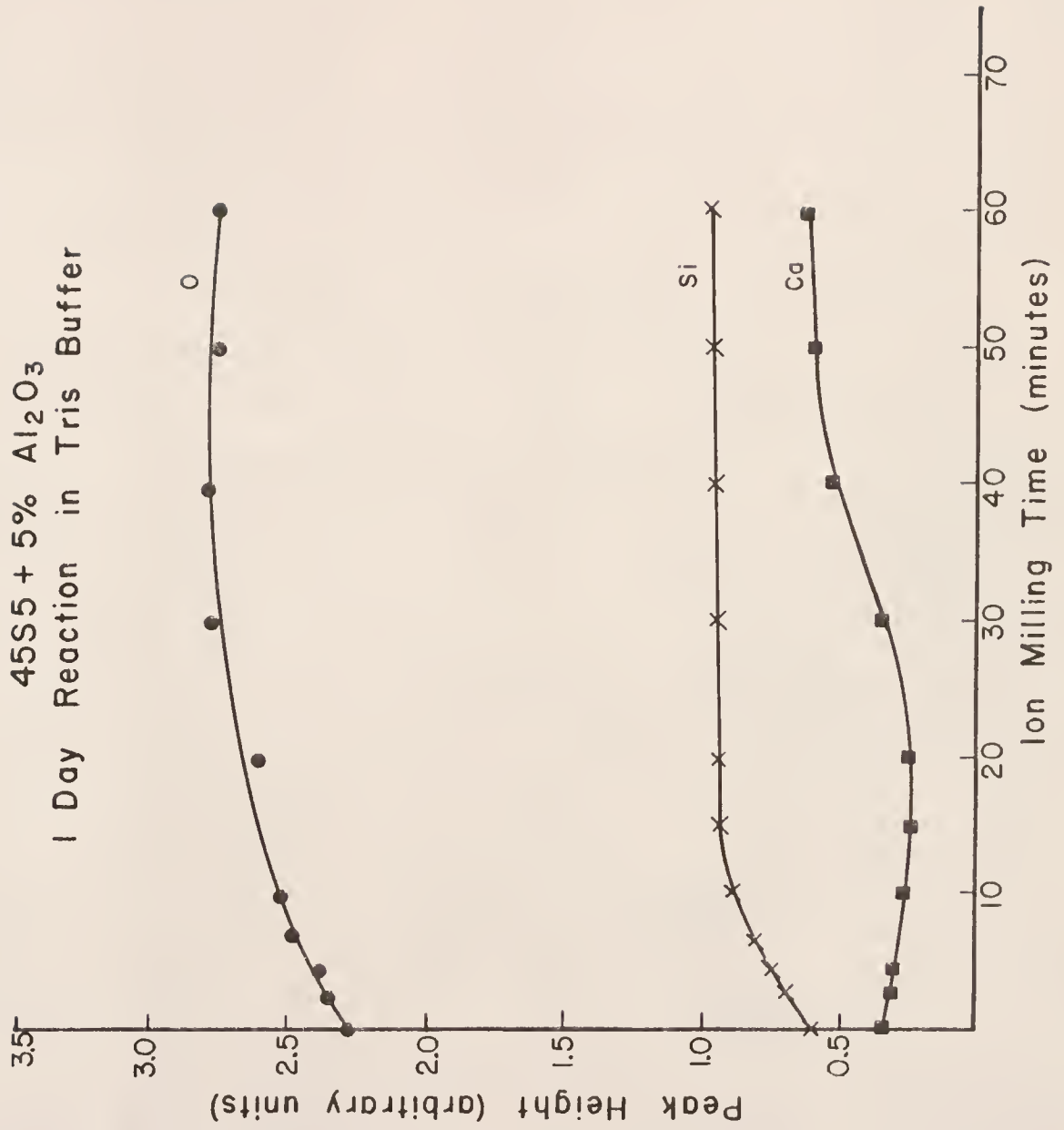


Figure 30. AES chemical profile for 45S5 + 5% Al₂O₃ bioglass reacted for 1 day in tris buffer.



a silica-rich glass surface. It can only be concluded that the alumina in the glass has caused a protective, nonreactive, silica-rich layer to form. Furthermore, the silica layer which has formed at the glass surface has prevented the formation of a calcium phosphate film. The absence of the calcium phosphate film has caused this glass to be nonbonding in the rat tibial model after 30 days. This result will be discussed further in Chapter V.

The difference in behavior between the alumina-containing bioglass and the double-coated alumina system can be explained with respect to the results presented in Figures 25, 26, 29 and 30. The increased Na and unusually high Ca level at the surface of the double-coated alumina (Figure 25) have allowed enough dissolution of the glass surface to form a thin calcium phosphate film over a slightly silica-rich layer (Figure 26). This behavior is similar to that observed in 45S5 bioglass [24]. However, the rate of formation has been slowed, presumably, by the presence of alumina. In comparison, the glass with the addition of alumina has formed a protective silica film, which prevents formation of a calcium phosphate surface layer.

Recent work on bioglass by Pantano and Hench [52] has led to the theory that the calcium phosphate film forms on a polymerizing silicic acid gel. The initial

formation of the silica gel apparently results from the solubilization of a sodium phosphate phase in the glass. While Figure 30 indicates that a sodium phosphate phase has, in fact, dissolved, the resulting silica rich phase has been altered by the alumina. This alteration is due to the fact that the alumina has decreased the number of nonbridging oxygens in the gel layer, thereby preventing the precipitation of the phosphate phase [52]. While this behavior would also be expected for the double-coated alumina, the initially high concentration of Ca and Na at the surface has partially offset the effect of the alumina in the coating. Thus, a calcium phosphate-rich surface film does form on the surface of the double-coated alumina samples.

Summary

A wide range of in-vitro surface reaction behavior has been demonstrated for the coated alumina system. The much lower reactivity of the single-coated alumina system is due to the large amount of alumina at the glass surface. Furthermore, the processing of the double-coated alumina has been shown to have an effect on the surface reactivity as well.

The presence of a calcium phosphate film on the double-coated alumina was demonstrated. This film was found to form more slowly than the film on the bulk

bioglass (3 days vs. 1-10 hours). SEM analysis showed the film to be uneven in its coverage of the sample surface. However, EDX and IRRS analyses showed the film to be very similar to that formed on the bulk bioglass.

Further analysis of the double-coated alumina surface revealed the presence of alumina at or near the surface (i. e., within 1 μm). To determine the role of the alumina on the surface reactivity of the glass, 45S5 and 5% Al_2O_3 glass was prepared for comparison with the coated alumina and bulk glass. The results of reactivity experiments with the alumina enriched glass showed no calcium phosphate film formation after 3 days of corrosion. Furthermore, in-vivo results discussed later show these glasses to be nonbonding in a rat tibial mini push-out model, also discussed later.

The lack of a calcium phosphate layer in the bioglass with 5% Al_2O_3 added can be explained on the basis of an alteration of the silica-rich reaction layer. Introduction of alumina into the silica-rich layer ties up nonbridging oxygens that would normally be available to bond with phosphate groups. This would then prevent a calcium phosphate buildup. The double-coated alumina was found to possess a surface initially rich enough in Ca and Na to permit the formation of a thin silica-rich gel layer. However, the presence of alumina within 1 μm of the surface has prevented the buildup of the silica-

rich layer to the 3-4 μm thickness normally found in the bulk bioglass. These results will be shown to be consistent with the in-vivo bone-bonding results presented in Chapter V.

CHAPTER IV

MECHANICAL PROPERTIES

Introduction

Ceramic materials, while quite brittle, often exhibit high mechanical strength. Due to this inherent brittleness, the use of ceramics in structural applications requires careful mechanical design. The development of bioglass and other ceramics which show good compatability in the biological environment has fostered considerable medical interest in ceramic materials. As mentioned earlier in this text, the use of fully dense Al_2O_3 ceramics as orthopaedic appliances is becoming widespread in Europe [12-14]. Many of these clinical studies have been in progress for over five years. No mechanical failures of the alumina implants have been reported. However, before the bioglass-alumina system can be considered as a clinically viable prosthetic system, its mechanical properties must be well characterized.

Alumina is one of the most inert oxide ceramics available. In addition, it has the strength requirements necessary to make it a potentially excellent candidate for a skeletal prosthetic device. However, as pointed out by Frakes, et al. [7], the information

concerning the mechanical properties of alumina, especially in biological environments is scarce. Of the information that is available, there is not yet full agreement on the reasons and mechanisms of failure. This is particularly true in the case of fatigue, aging, and delayed failure of alumina.

In one of the earliest studies on delayed failure of alumina, Pearson [53] reported strengths of 99.5% Al_2O_3 to decrease by 25% under constant tensile load conditions in ambient air. Duration of the tests was on the order of 10^5 seconds. Furthermore, he noted that tests in vacuum under constant load resulted in no significant decrease in strength. Thus, he concluded that the delayed failure of the Al_2O_3 was due to chemical attack of the stressed materials by water in the ambient air. The results of Pearson were substantiated by Williams [54] at about the same time. Conducting both delayed fracture (failure) and cyclic fatigue experiments, he found the delayed fracture strength of 99% Al_2O_3 to be 78% of the single stroke strength of 255 MPa. Furthermore, he found that the cyclic fatigue survival stress was only 57% of the single stroke strength. This survival stress level occurred at 10^7 cycles, and should properly be termed an endurance limit.

In more recent works, Sarkar and Glinn [55] found static fatigue (delayed failure under constant load)

and cyclic fatigue mechanisms to be operative in Lucalox and Sintox aluminas. They showed that both aluminas failed at lower stress levels when subjected to cyclic loads than when loaded statically. Their conclusions that both delayed failure and cyclic fatigue mechanisms normally operate on Al_2O_3 agree with the conclusions of Williams. However, Sarkar and Glinn also show cyclic fatigue effects under dry argon and liquid nitrogen conditions, contradicting the conclusions of Pearson [53]. Furthermore, they conclude that a fatigue limit of 50% of the bend strength is practical for these materials which is somewhat lower than that reported by Williams [54].

Krohn and Hasselman [56] also reported on the delayed failure of Al_2O_3 . They found a delayed failure strength of 70% of the bend strength of the alumina, which they refer to as a static fatigue limit. Furthermore, they reported that the amplitude and frequencies of stress used in cyclic fatigue work definitely affected the results. They showed that for a given applied stress an increase in frequency of that stress could decrease the time-to-failure by an order of magnitude. While they agreed with Williams [54] that cyclic fatigue effects will dominate static fatigue effects at low stress levels, they noted that for high stress levels and short durations of load static fatigue

mechanisms might be dominant. Krohn and Hasselman also pointed out that due to the large number of possible mechanisms operating under conditions of cyclic fatigue, no satisfactory theory could be developed to explain the observed phenomenon.

Sedlacek and Halden [57] reported even greater decreases in the delayed failure strength of high purity Al_2O_3 . They reported a delayed failure strength of 60% of the bend strength. Below this limit they found no failures. It should be noted, however, that the duration of testing was only 24 hours.

Kirchner and Walker [58] studied delayed failure and cyclic fatigue of Al_2O_3 with compressive surface layers. They found no difference in the mechanism of stress corrosion fatigue in the groups with and without compressive surface layers. In certain cases, they interrupted the delayed failure test and measured short-time strength. They observed this strength to be as great as those samples not subjected to the delayed failure test. They therefore concluded that the stress corrosion mechanism could not simply be the slow growth of preexisting cracks as put forth by Pearson [53].

From the information above, it is clear that there is not yet full agreement as to the mechanisms of delayed failure of Al_2O_3 ceramics. Furthermore, the use of fatigue experiments for engineering design of

ceramic materials is highly dependent on the test conditions employed (e. g., frequency, amplitude of stress, atmosphere). Therefore, attention has recently turned to the use of fracture mechanics theory as a method of determining and predicting the mechanical properties of ceramics.

In addition to providing a more fundamentally sound method of assuring mechanical reliability, the use of fracture mechanics appears to be making great progress in aiding the understanding of brittle fracture processes. Davidge, et al. [59] have developed strength probability-time diagrams as an aid for the design when using engineering ceramics. These diagrams are easily generated from measurements of the strain rate dependence of the fracture strength. Evans [60] has predicted time-to-failure based on measurement of slow crack growth in ceramics (crack velocity vs. stress intensity). Evans and Wiederhorn [61] have successfully applied basic fracture mechanics theory with crack velocity vs. stress intensity measurements to develop proof-test diagrams for certain glass and ceramic materials. From these examples, it is clear that fracture mechanics theory has provided the background necessary for making reliable lifetime predictions for implant materials.

While the techniques described above are useful for most ceramic materials, they rely mainly on the

monitoring of artificially induced cracks. These methods are not particularly suited to analysis of coated systems such as the bioglass-coated alumina discussed in this text. Ritter and Meisel [62] have developed an alternative method for assuring mechanical reliability which is particularly attractive for studying the bioglass-coated alumina system. It embodies the basic fracture mechanics theories provided in the works of Evans and Wiederhorn [60, 61, 63] while utilizing simple strength tests to provide the necessary data for making lifetime predictions.

It is the object of this study to apply the theories of Evans and Wiederhorn as modified by Ritter and Meisel [62] in order to be able to predict minimum lifetimes of the bioglass-coated alumina system. In addition to generating lifetime prediction diagrams, this study will compare the mechanical behavior of uncoated alumina with coated alumina using standard cyclic fatigue methods. By comparing these two methods, valuable information about stress corrosion susceptibility and mechanisms of failure can be gained.

A Method for Determining Lifetime Prediction Diagrams

As already mentioned, the technique of making long-term lifetime predictions is founded in fracture mechanics theory. This theory develops from the

reasonable assumption that fatigue failure of ceramics occurs from the stress-enhanced growth of preexisting flaws to dimensions critical for spontaneous fracture. Thus, the crack velocity, V , during this period of subcritical crack growth can be expressed as a power function of the stress intensity factor K_I by the relation:

$$V = AK_I^N \quad (3)$$

where A and N are constants related to material properties. N is a measure of the stress corrosion susceptibility of a given material. Typical values of N for ceramic materials range from 10-20 for glass [62, 63] to 30-50 for aluminum oxides and silicon carbides [60, 61]. As crack velocities are of the order of 10^{-7} - 10^{-14} m/sec. for ceramics, A is a very small number, generally 10^{-50} - 10^{-90} as reported in the literature [63].

As shown in the Appendix, the fracture strength at a constant stressing rate can be derived from Equation (3). The result yields:

$$\sigma_f^{N+1} = \left[\frac{2}{AY^2(N-2)K_{IC}^{N-2}} \right] (N+1) \sigma_{IC}^{N-2} \dot{\sigma} \quad (4)$$

where σ_f is the fracture strength, $\dot{\sigma}$ is the stressing rate, K_{IC} is the critical stress intensity factor, σ_{IC} is the strength of the material in an inert environment, and

Y is a constant related to flaw geometry. This equation has been rewritten by Ritter [62] as:

$$\log \sigma_f = \frac{1}{N+1} \left[\log B + \log(N+1) + (N+2)\log\sigma_{IC} + \log \dot{\sigma} \right] \quad (5)$$

where B is equal to the expression in brackets in Equation (4). Using Equation (5), the crack growth parameters B and N can be determined from a log-log plot of the average fracture strength, σ_f , as a function of stressing rate, $\dot{\sigma}$. The slope of such a plot is equal to $\frac{1}{N+1}$ with an intercept which gives B .

An expression for the time-to-failure can also be derived from Equation (3), and is given by Ritter [62] as:

$$t_f = B \sigma_{IC}^{N-2} \sigma_a^{-N} \quad (6)$$

where t_f is the time to failure for a given applied stress σ_a , B and N are the crack growth parameters, and σ_{IC} has been defined above. The derivation of this equation is also given in the Appendix.

The probability of failure (F) of a piece for a given t_f and σ_a can be obtained from Equation (6) by expressing the inert strength (σ_{IC}) in terms of its failure probability. This assumes that the minimum inert strength will yield the minimum value for t_f , etc.

Ritter [62] has shown that this distribution can be given by the following Weibull relationship:

$$\ln \left[\ln \frac{1}{1-F} \right] = m \ln \frac{\sigma_{IC}}{\sigma_0} \quad (7)$$

where m and σ_0 are constants related to the inert strength distribution. Thus, by coupling the Weibull distribution, Equation (7), with Equation (6), the failure probability for a given lifetime under a constant applied tensile stress can be calculated.

An additional method to safely predict the lifetime of ceramics is to use a proof test. In proof testing, samples are subjected to stresses that are greater than those expected in service. This method of testing insures that weak samples will be eliminated, and that the remaining samples will have a minimum strength. This implies that those samples which pass the proof test will have a minimum lifetime with no failures. By substituting a proof test stress (σ_p) for σ_{IC} in Equation (6), Ritter [64] has shown that the minimum lifetime after proof testing (t_{min}) is:

$$t_{min} = B \sigma_p^{N-2} \sigma_a^{-N} \quad (8)$$

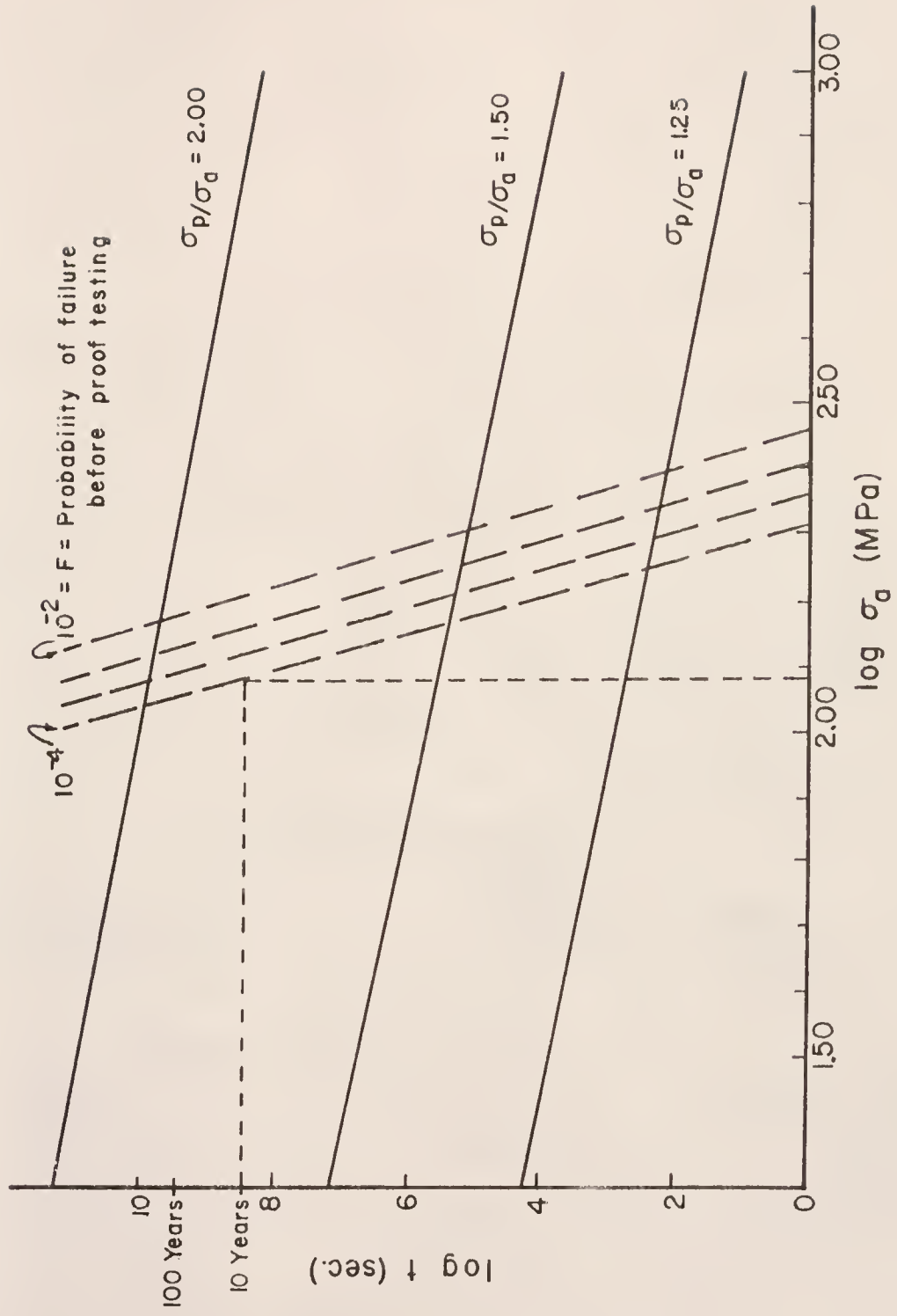
Thus, Equations (7) and (8) give lifetime predictions both before and after proof testing, and are dependent

on the inert strength distribution and the crack growth parameters B and N . These lifetime predictions are most easily grasped if presented in the form of a lifetime prediction diagram. By plotting $\log t$ vs. $\log \sigma_a$, and generating a series of lines of various proof test stress to service stress ratios (σ_p/σ_a), it is possible to determine what proof test stress would be necessary to insure a minimum lifetime for a given service stress (σ_a).

Figure 31 represents a typical lifetime diagram. By way of example, to insure that no samples will fail within 10 years under an applied service stress of 126 MPa (18,000 psi), a proof test stress 1.80 times as large as the service load must be used. This σ_p/σ_a ratio is found simply by the intersection of the lines which represent the given service conditions. By using the Weibull relation and plotting various failure probabilities (F), it is possible, without proof testing, to insure that only a certain fraction of pieces under a given load will fail within a given period of time. Using Figure 31 as an example, for an expected lifetime of 10 years and an applied stress of 126 MPa, the failure probability is 10^{-4} . That is, 1 sample in 10,000 will fail before 10 years under the given service stress.

Figure 31. Typical lifetime prediction diagram.

Sample Lifetime Prediction Diagram



Procedures

Samples for mechanical testing were chosen from the results of studies obtained in Chapter II and Chapter III. The final selection of samples was based upon the in-vitro corrosion response. Due to the large number of specimens necessary for mechanical testing, only one of the coated systems was chosen. The bioglass-coated system which most closely approximated the in-vitro response for bulk bioglass (45S5) was selected. The processing followed the procedure outlined in Chapter II. Firing schedules for the coated alumina system are shown in Table 6. After firing and cooling, samples were placed in a dessicator until testing.

All mechanical studies, except the in-vivo studies, employed the use of the biaxial flexure method developed by Wachtman, et al. [65]. This method involved supporting a thin, circular disc on three equally spaced ball bearings and applying a concentric load at the center of the support circle. Figure 32 shows such an apparatus schematically. One advantage of this test method is that slightly warped samples may be used without affecting the results. In addition, Wachtman, et al. [65] has shown that relatively small numbers of samples may be used to generate statistically significant data. As only the area of the sample within the support circle is loaded, any deleterious edge effects are eliminated.

Table 6

Firing Schedule for Preparing Double-Coated
Alumina Samples for Mechanical Testing

<u>Temperature</u> <u>°C</u>	<u>Time</u> <u>(min.)</u>	<u>Temperature</u> <u>°C</u>	<u>Time</u> <u>(min.)</u>
1350 ⁰	15	----	--
1350 ⁰	15	1150 ⁰	30

Note: All samples were heated from room temperature to 1000⁰ C at 15⁰ C/min. Samples were cooled at 8⁰ C/min.

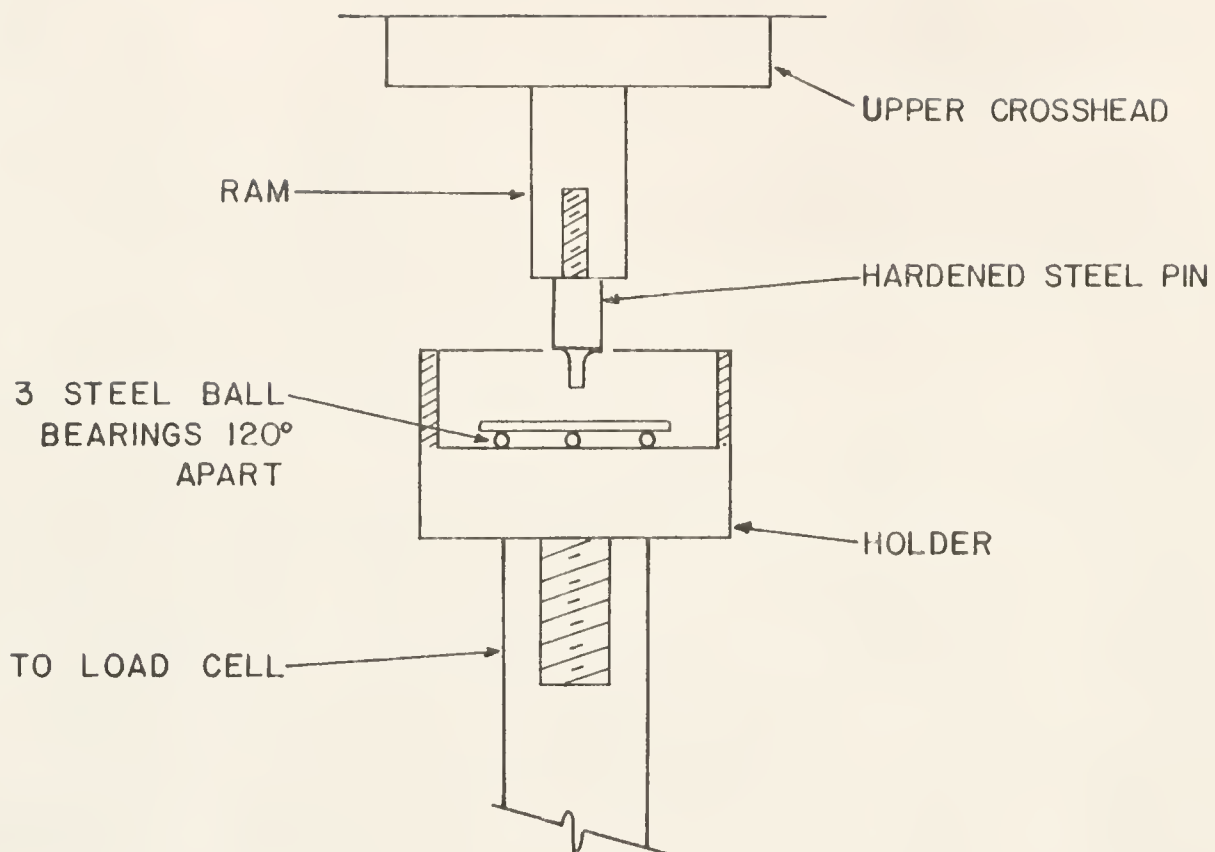


Figure 32. Schematic diagram of biaxial flexural testing apparatus.

Samples are easily fabricated and the coated portion of the specimen may be exposed to physiologic solution while under stress.

Cyclic fatigue tests were conducted using an MTS* fatigue testing machine. This is a closed loop system capable of applying cyclic loads of up to 135 MPa at frequencies ranging from 1 Hz to 1100 Hz. Frequencies of 1 to 5 Hz were used in these studies. In all cases a sinusoidal wave form was used in applying load. Constant tension preloads were applied to the specimens and a given load then cycled about the mean. Tests were carried out in air (20⁰ C, R.H. 70%) and in simulated physiologic solution at 37⁰ C. The temperature was maintained by using heating strips attached to the sample holder. Temperatures of the solution were measured using a standard laboratory thermometer.

Stressing rate experiments were carried out using a universal testing machine.** At least five stressing rates were used for each experiment. Stressing rates ranged from 45 MPa/sec. to 450 MPa/sec. Samples were tested in air (20⁰ C, R.H. 70%), and in physiologic solution at room temperature. The crack growth parameters from these experiments were calculated from the $\log \sigma_f$

* MTS Corp., Minneapolis, Minnesota.

** Instron Corp., Greenville, North Carolina.

vs. $\log \dot{\sigma}$ plots as described in the previous section. All data were fitted to straight lines using the least squares method of linear regression.

Inert strengths of both double-coated and uncoated alumina were determined in a dry N_2 atmosphere. Figure 33 is a schematic diagram showing the method employed. The N_2 gas was pumped through a copper cold trap (liquid N_2) to remove any water vapor in the gas. The dry N_2 was then pumped through more copper tubing submerged in water to heat the gas back to room temperature.

The gas then entered the testing chamber. A positive pressure of N_2 gas in the chamber was maintained throughout testing. Dry N_2 was chosen over liquid N_2 for inert environment testing mainly due to the fear that a large decrease in temperature might induce stresses at the glass-alumina interface. This condition would arise due to the different thermal expansion coefficients of the two materials and might conceivably lead to erroneous results. However, a number of uncoated alumina samples were tested in liquid N_2 to serve as reference for dry N_2 testing.

After inert strengths and stressing rate data were collected, lifetime prediction diagrams were generated. The details of this procedure are given in the previous section and the Appendix. After construction of the lifetime prediction diagrams, samples were

Processing of Dry N₂ Gas

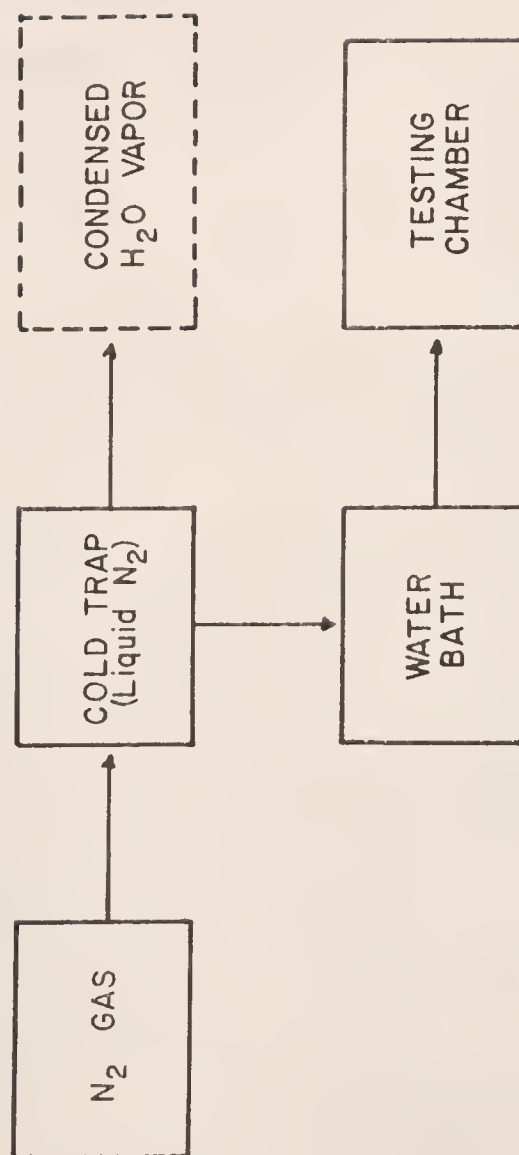


Figure 33. Schematic diagram showing processing of dry N₂ gas.

subjected to proof testing. Proof test loads and expected service loads were chosen at unusually high levels so that the expected lifetime of the pieces subjected to proof testing would be relatively short. This was done so that pieces could be statically loaded after proof testing to determine that they would, in fact, survive the predicted lifetimes.

In addition to the in-vitro testing, the mechanical strength of double-coated alumina rods implanted in dog fibulae were also tested. The rods were 4 cm long and .3 cm in diameter. Using sterile surgical procedures, a 4 cm long section of the dog fibula was removed while the dog was under anesthesia, and a rod implanted in the space. The musculature around the fibula was utilized to maintain the position of the implant.

Due to the expense and long duration of the experiments, only a very limited number of samples were tested. Six samples each were tested after 12 weeks and 24 weeks of implantation. The tests were conducted within 24 hours of sacrifice of the animal. After sacrifice, all test pieces were kept in a 4% gluteraldehyde solution until testing. As the samples were cylindrical, a standard 4 point bend test was conducted using a universal testing machine. A stressing rate of 45 MPa/sec was used for all samples. For comparison, one

group of 12 double-coated alumina rods was tested in 4 point bending with no implantation.

Results and Discussion

Fatigue of Coated and Uncoated Al_2O_3

The results of the cyclic fatigue tests are presented in Figures 34-37. Each sample is represented by a single data point on the curves, except where parentheses are found. In these cases the numbers in parentheses represent the number of samples tested at each point. The crosses denote the average of the number of cycles to failure for each stress level. The solid lines denote the upper and lower bounds of the observed cyclic fatigue.

The data presented in the fatigue curves reveal that only one uncoated alumina sample out of nine failed after 10^7 cycles at a stress of 175 MPa (25,000 psi) cycled about a mean stress of 104 MPa (15,000 psi). In addition, no double-coated alumina samples failed at this stress level. In comparison, more than half of the samples, both double-coated and uncoated, cycled at 206 MPa (30,000 psi) about a mean stress of 104 MPa failed during the test. Examination of the average values obtained for the number of cycles to failure shows that the bioglass-coated alumina samples withstood more cycles at a given stress level than did the uncoated

Figure 34. Cyclic fatigue of double-coated alumina, tested in air
at 200 C, relative humidity - 70%.

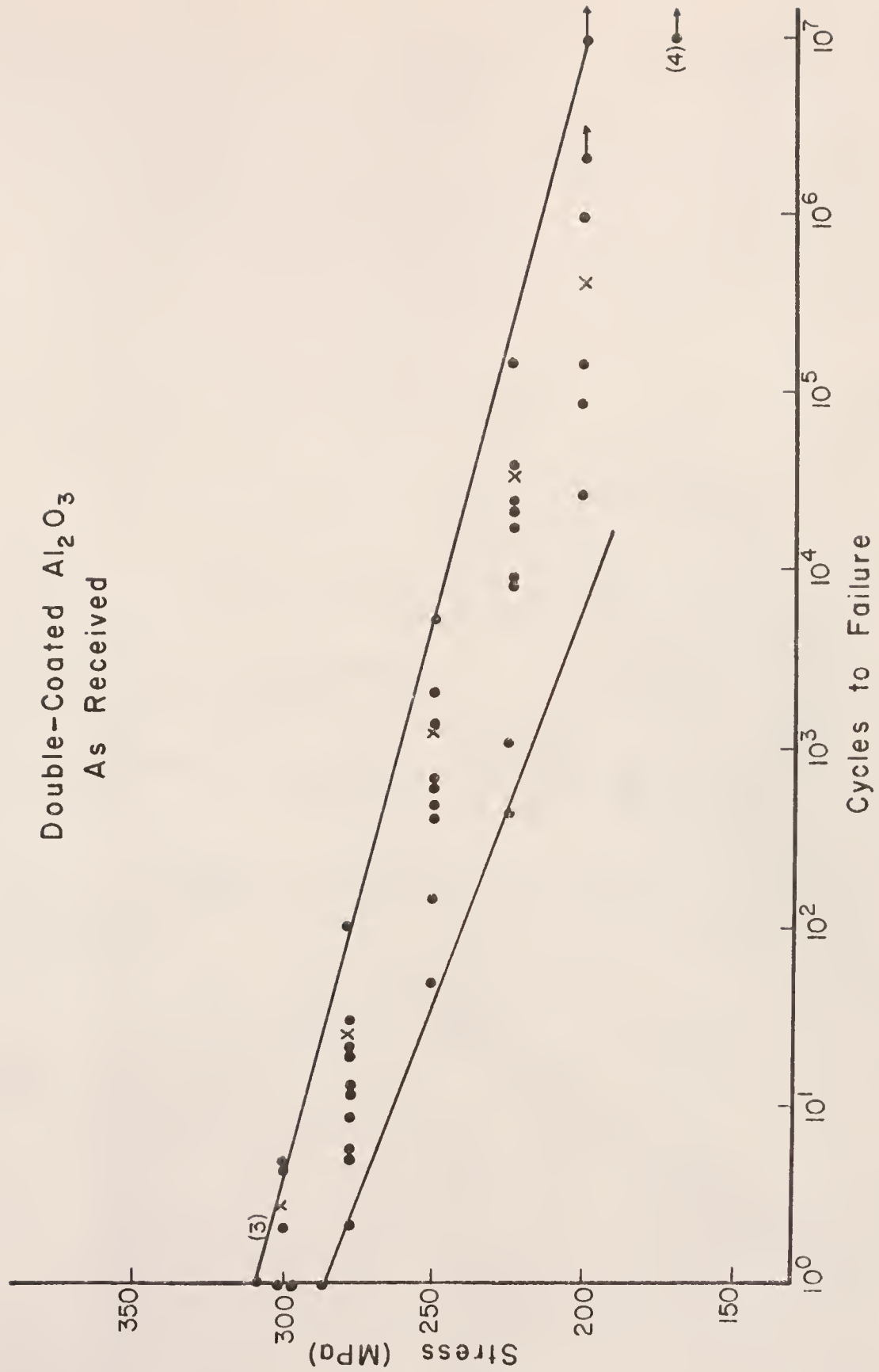


Figure 35. Cyclic fatigue of uncoated alumina, tested in air
at 20° C, relative humidity - 70%.

Uncoated Al_2O_3
As Received

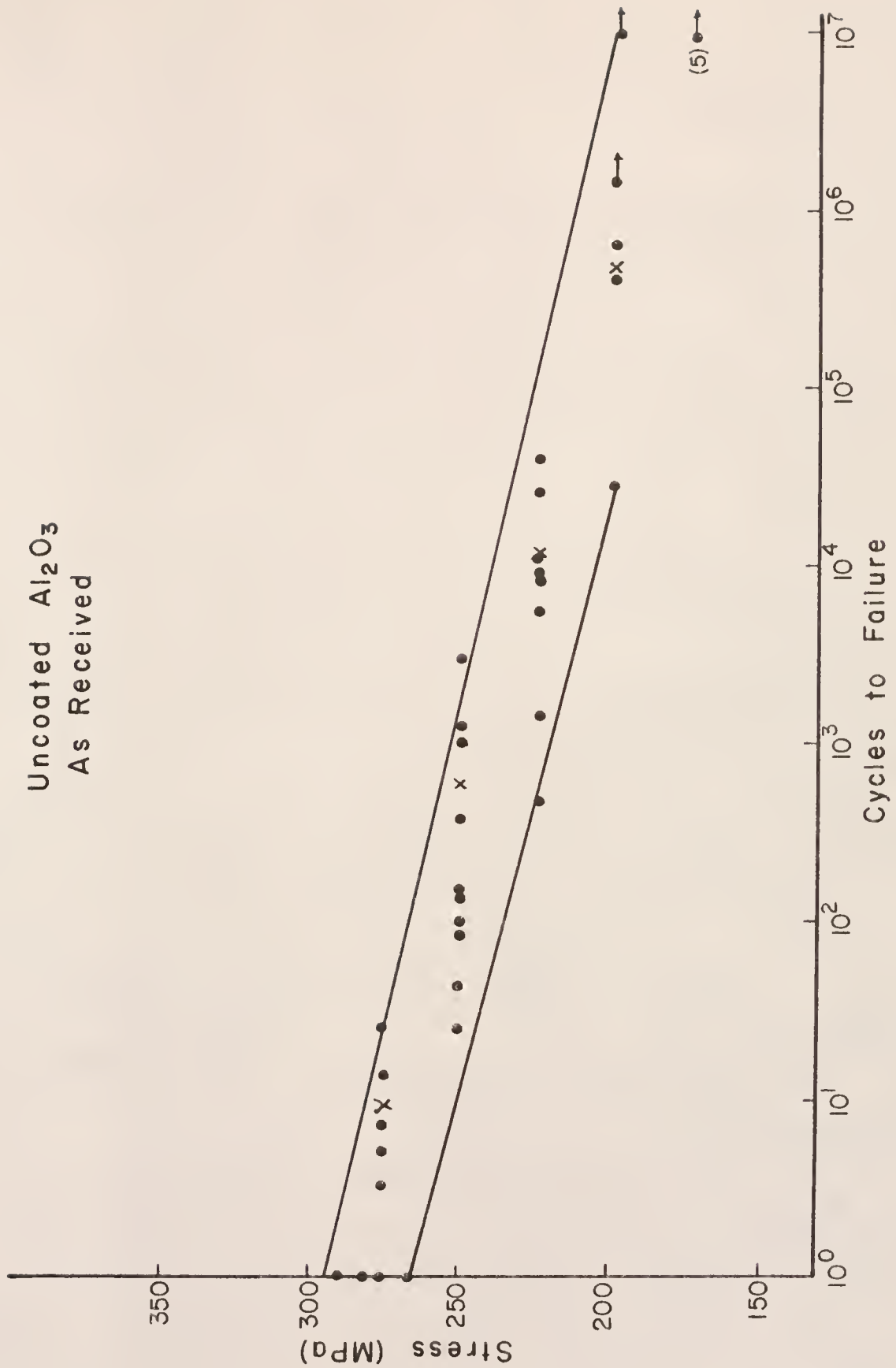


Figure 36. Cyclic fatigue of double-coated alumina, tested in tris buffer at 37° C.

Double-Coated Al_2O_3
In Tris Buffer - 37°C

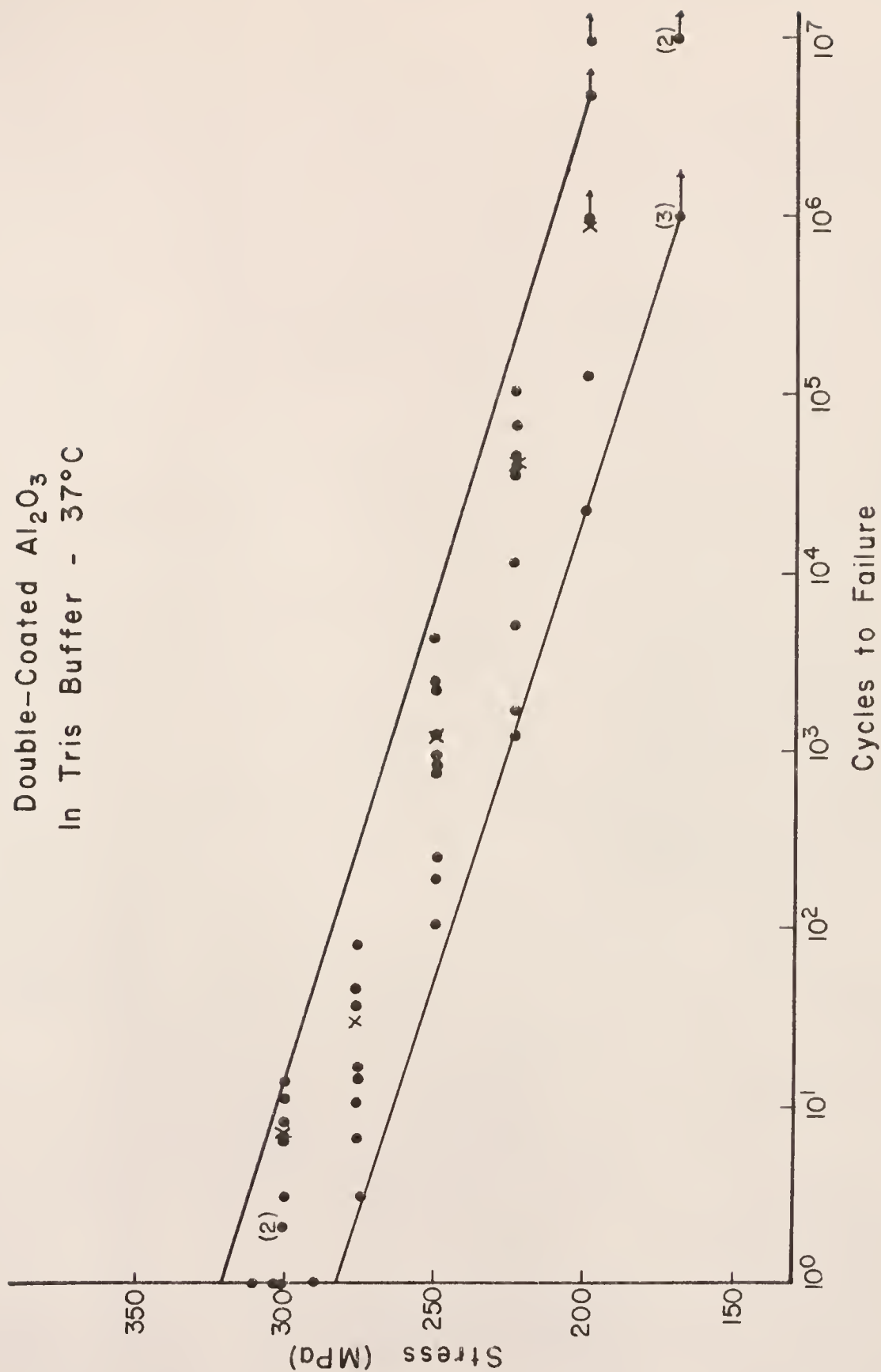
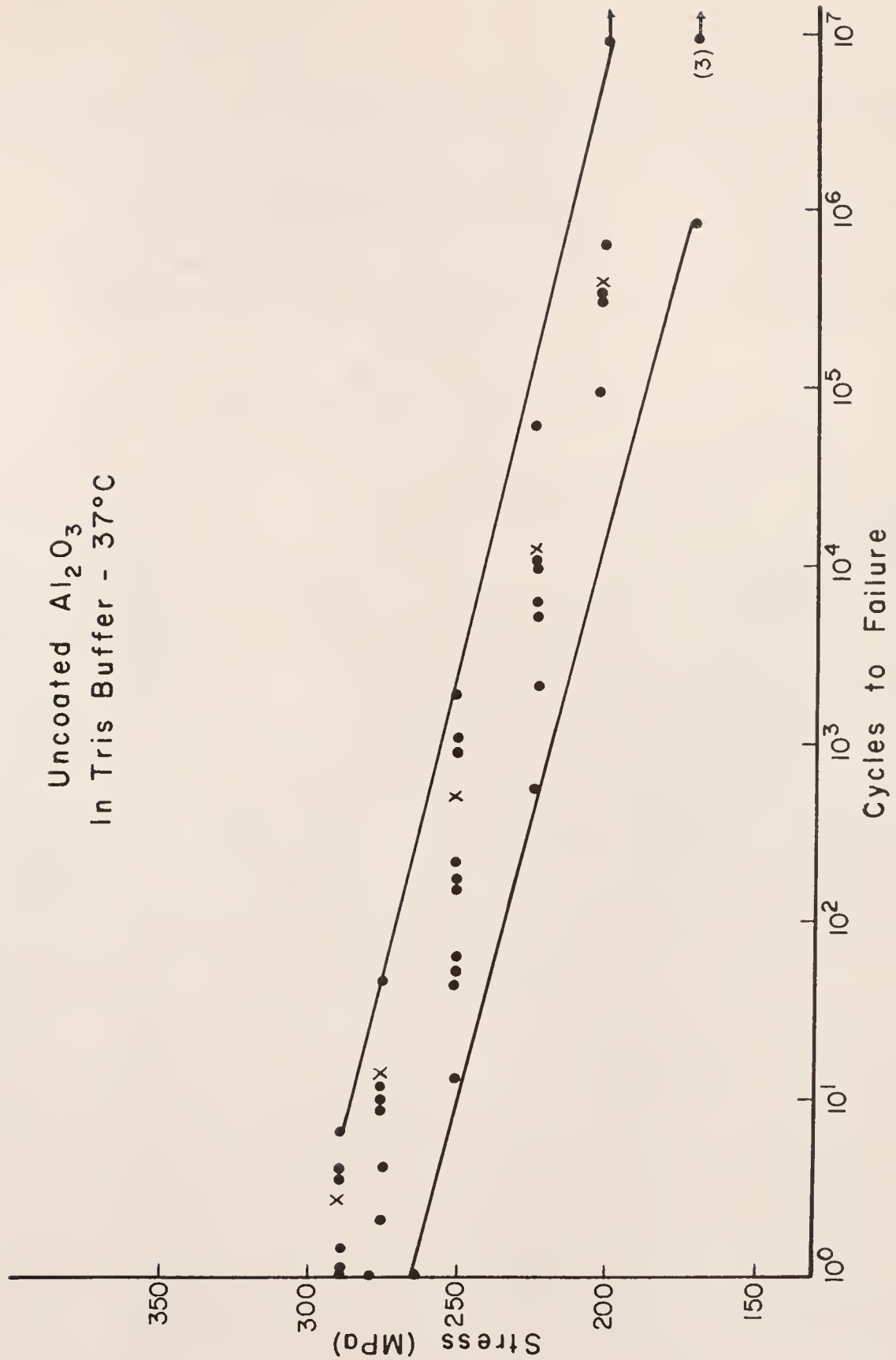


Figure 37. Cyclic fatigue of uncoated alumina tested in tris buffer at 37° C.

Uncoated Al_2O_3
In Tris Buffer - 37°C



alumina. The trend is found to hold for samples tested in tris buffer as well as for those tested in air. These data also show a slight decrease in the average values of cycles-to-failure for samples tested in tris buffer when compared to those tested in air.

From these results, an endurance limit of approximately 190 MPa (27,500 psi) at 10^7 cycles with a 90% probability of survival for both the uncoated and double-coated alumina seems reasonable. It is also evident that the coating process has caused an increase in the average number of cycles-to-failure, both in tris buffer and in the ambient. This is most evident at the higher stress levels. For example, at 250 MPa (36,000 psi), the average cycles-to-failure for coated alumina in tris buffer is 1300. This is compared to 750 cycles for uncoated alumina in tris buffer. Thus, the coating is increasing the short term fatigue resistance of the alumina, especially at high stress levels.

Two points must be made with regard to the test results conducted in tris buffer. First is the fact that no difference was found between the endurance limit of the samples tested in the physiologic buffer as compared to those tested in air. This result is particularly important as Frakes, et al. [7] have shown large decreases in strength of porous alumina when tested in bovine serum and water over that tested in air.

The second point to be made is that the increase in test temperature from 22⁰ C to 37⁰ C had no effect on the cyclic fatigue strength. These results agree with the early work of Williams [54], who found no effect of temperature up to 900⁰ C on the cyclic fatigue strength of alumina. In contrast to Williams work, Chen and Knapp [66] found a decrease in the strength of 96% alumina with temperatures up to 219⁰ C, although there was no substantial change in the fatigue strength noted between 20⁰ C and 50⁰ C.

Aging Effects

In addition to the in-vitro fatigue experiments presented above, the effects of aging of the coated alumina were studied. The results of the mechanical testing of the dog fibulae are presented in Table 7. The results show a statistically significant decrease in the bend strength of the double-coated alumina rods after implantation when compared to the bend strength of the same material tested in air. The strength of the coated rods after implantation as presented in Table 7 was found to be 207 MPa (30,000 psi), which is 82% of the bend strength of the same material tested in air (248 MPa). The data also showed that there was no statistical difference between the strength of the rods implanted for 12 weeks and 24 weeks. Results of the student's "t" test [67] showed no significant

Table 7
Fracture Strength of Double-Coated
Al₂O₃ Dog Fibulae

<u>12 Weeks</u>	<u>24 Weeks</u>
$\bar{x}$ = 211 MPa	$\bar{x}$ = 202 MPa
σ = 20 MPa	σ = 25 MPa
$\frac{\sigma}{\bar{x}}$ = 9%	$\frac{\sigma}{\bar{x}}$ = 11%
n = 6	n = 6

Pooled Data

$\bar{x}$ = 208 MPa
 σ = 19 MPa
 $\frac{\sigma}{\bar{x}}$ = 8%
 n = 12

Double-Coated Alumina Rods
Nonimplanted

$\bar{x}$ = 248 MPa
 σ = 21 MPa
 $\frac{\sigma}{\bar{x}}$ = 9%
 n = 12

difference in the mean strength of the two groups of implanted rods at the 95% confidence limit.

The data suggest that the observed 18% decrease in strength of the rods may be a delayed failure (fatigue) effect. However, there is no evidence that the rods were loaded in tension during implantation. X-rays taken during the experiment show the rods in various positions with respect to the sagittal (vertical) plane of the fibulae. Thus, it seems more likely that the decrease in strength was due to environmental aging of the material in the body rather than a fatigue effect.

To test this possibility, 40 double-coated alumina discs were placed 20 each in 200 ml tris buffer and distilled water. The samples were aged at 37⁰ C for 1000 hours. After aging, the samples were tested in biaxial flexure at a stressing rate of 45 MPa/sec. The results showed a flexural strength of 212 MPa with a variance of 9% for samples tested in tris buffer and water as compared to unaged strengths of 256 MPa with a variance of 6%. Thus, it seems likely that the decrease in strength of the implanted rods was due to an aging effect. While the aging effect observed here was also observed by Frakes, et al. [7], the decrease in strength of the porous alumina was found to be proportionately greater than that observed in the present study. Furthermore, these results indicate no difference in the

aging of coated alumina when tested in simulated physiologic solution as compared to the aging effect found in-vivo.

Lifetime Prediction Diagrams

The first step in producing lifetime prediction diagrams is to obtain the crack growth parameters B and N . As mentioned in the description of the method for determining lifetime prediction diagrams, B and N can be obtained from a plot of the average fracture strength as a function of stressing rate. The results of these tests are presented in Figures 38 and 39 for double-coated alumina and uncoated alumina, tested in air and in tris buffer.

The results in Figure 38 show that the coated alumina has a higher fracture strength at all stressing rates than does the uncoated alumina. In addition, the slope of the line for the coated system is greater than for the uncoated system, resulting in a lower value of N for the coated system. Notice that the value for $\log B$ is greater for the coated system. From the bracketed term in Equation (4), which gives an expression for B , it is clear that a decrease in N should lead to the observed increase in B for the coated samples assuming K_{IC} remains constant.

The trends observed from study of Figure 38 also apply to Figure 39. However, the magnitude of the difference in the strength of coated vs. uncoated

Figure 38. Fracture strength as a function of stressing rate for uncoated and double-coated alumina, tested in air.

Double-Coated Al_2O_3 vs. Uncoated Al_2O_3

In Air (R.H. ~70%, R.T. 22°C)

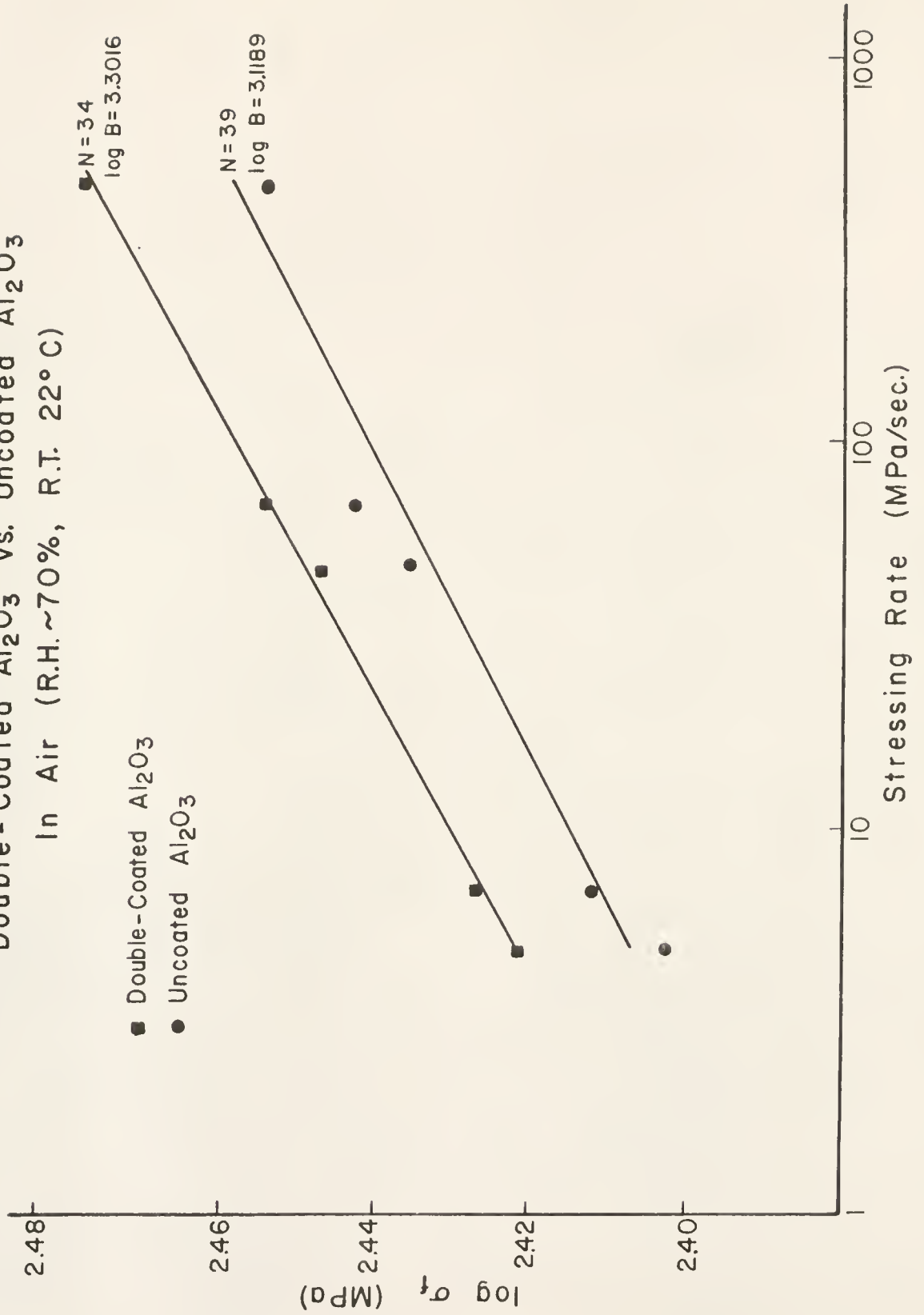
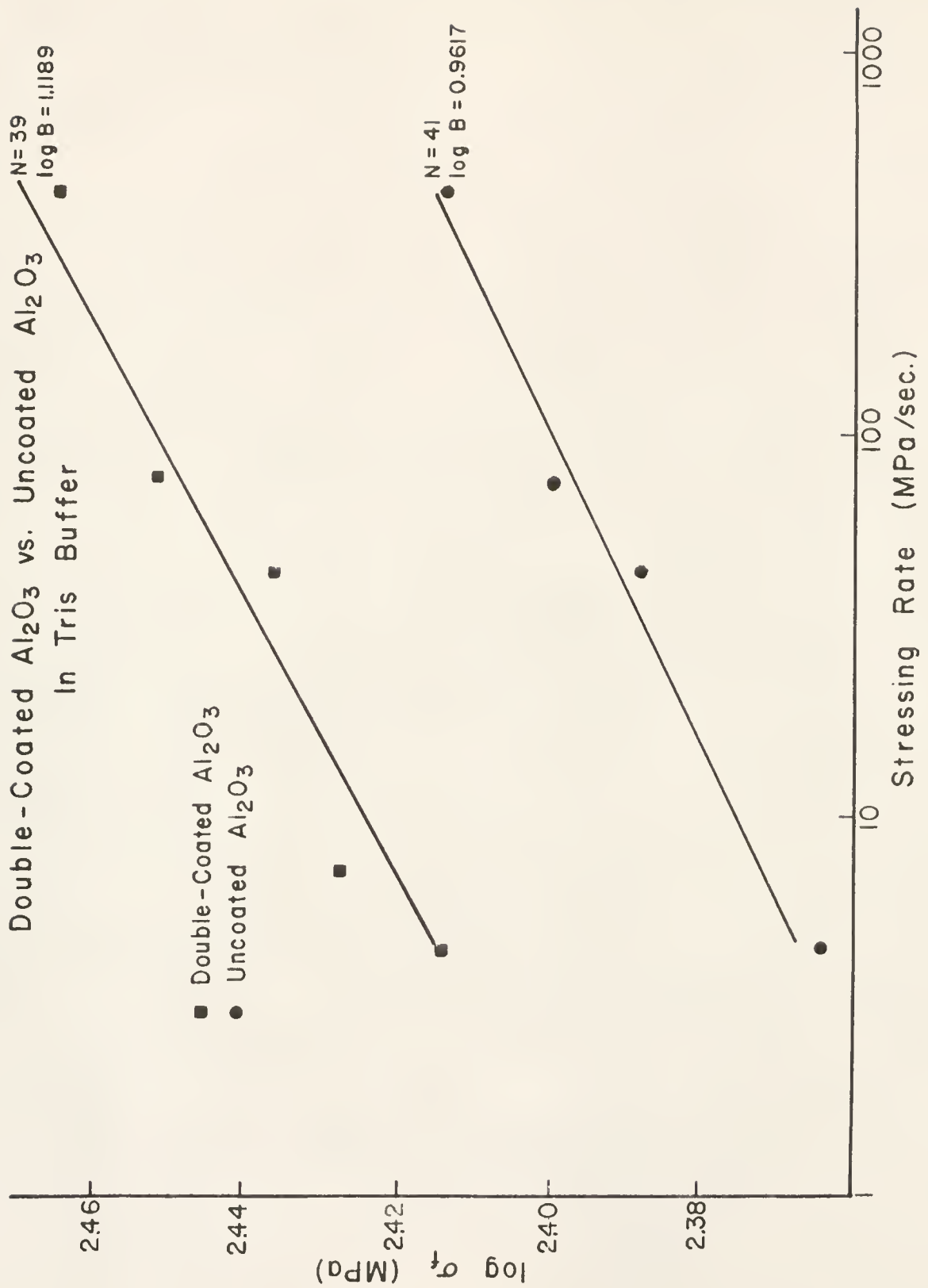


Figure 39. Fracture strength as a function of stressing rate for uncoated and double-coated alumina, tested in tris buffer.



alumina has increased in the tris buffer. Furthermore, the slopes of the lines are more nearly equal in Figure 39 than in Figure 38. Comparison of Figures 38 and 39 show that the uncoated alumina has incurred a larger decrease in strength than has the coated alumina. This tendency was also in evidence in the cyclic fatigue testing presented in the previous section. Recall that the average cycles-to-failure for the coated alumina was slightly higher than for uncoated alumina.

To determine whether the increase in strength observed in the coated alumina system was due to some residual stress remaining from processing, or due to a change in the material system, samples were tested in both liquid N_2 and dry N_2 gas. Testing in these two media provided an inert atmosphere and two very different test temperatures. Thus, any residual stresses which existed in the material at room temperature would change as the samples cooled to liquid N_2 temperature. As water was not available to induce stress corrosion during testing, any differences in the observed strengths could be linked to changes in the residual stresses of the material.

Table 8 shows the results of the tests for both coated and uncoated alumina. Applying student's "t" test [67] to both groups of data showed no significant difference (95% confidence limit) in the mean value of the dry N_2 strengths vs. liquid N_2 strengths. However,

Table 8
Inert Atmosphere Testing

	Double-Coated Al_2O_3		Uncoated Al_2O_3	
	Dry N_2	Liquid N_2	Dry N_2	Liquid N_2
$\bar{x}$ (MPa)	398	385	347	340
σ (MPa)	40	32	18	21
$\sigma/\bar{x}$ (%)	11.6	8.2	5.4	6.1
n	19	21	29	38

Note: Tests performed at both 450 MPa/sec. and 66 MPa/sec.

for both dry N_2 and liquid N_2 , there was a significant increase in strength for coated alumina over uncoated alumina. These results show that there are no residual stresses of any consequence in the coated alumina system. Furthermore, the inert atmosphere testing clearly accentuates the strength increase in the coated alumina system which was observed to occur in Figures 38 and 39.

The resulting values for B and N of Figure 38 and 39 were substituted into Equation (8) to calculate lifetime prediction diagrams. Figures 40 and 41 are prediction diagrams for the uncoated and coated alumina system tested in air. Figures 42 and 43 are diagrams for the same systems tested in tris buffer. It should be pointed out that as no effect of temperature was found in cyclic fatigue testing, all tests used to construct lifetime diagrams were performed at room temperature. The data points on the various diagrams were calculated by picking various σ_p/σ_a ratios and calculating a t_{min} for various given σ_a 's.

The four prediction diagrams presented are very similar to each other in appearance. However, examination of any given σ_p/σ_a line for the four diagrams shows that each intercepts the y axis at different points. Table 9 presents this situation more clearly. The calculated σ_p/σ_a ratio was obtained by choosing an in-service applied stress of 104 MPa and a guaranteed lifetime of

Figure 40. Lifetime prediction diagram for double-coated alumina,
tested in air.

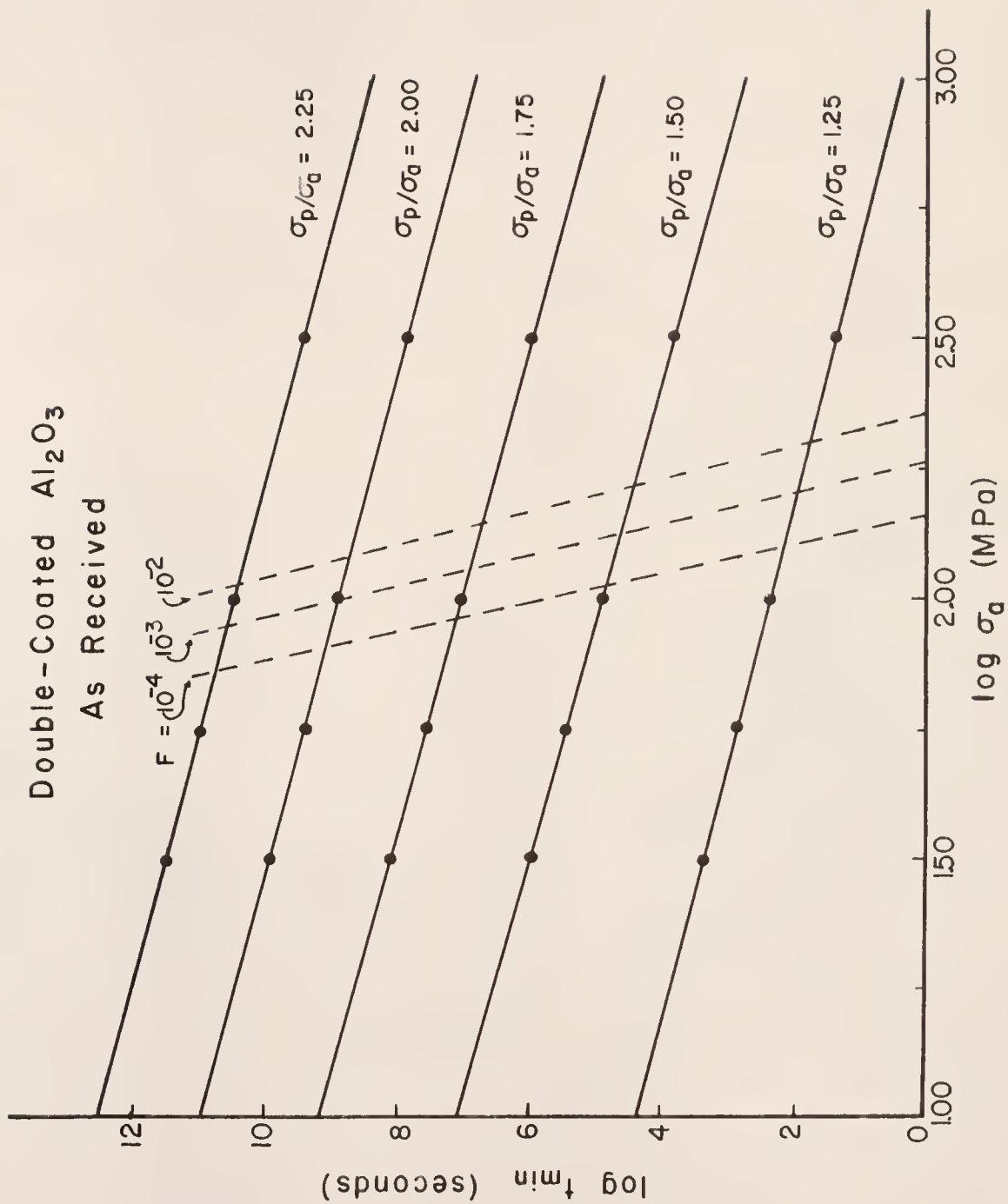


Figure 41. Lifetime prediction diagram for uncoated alumina,
tested in air.

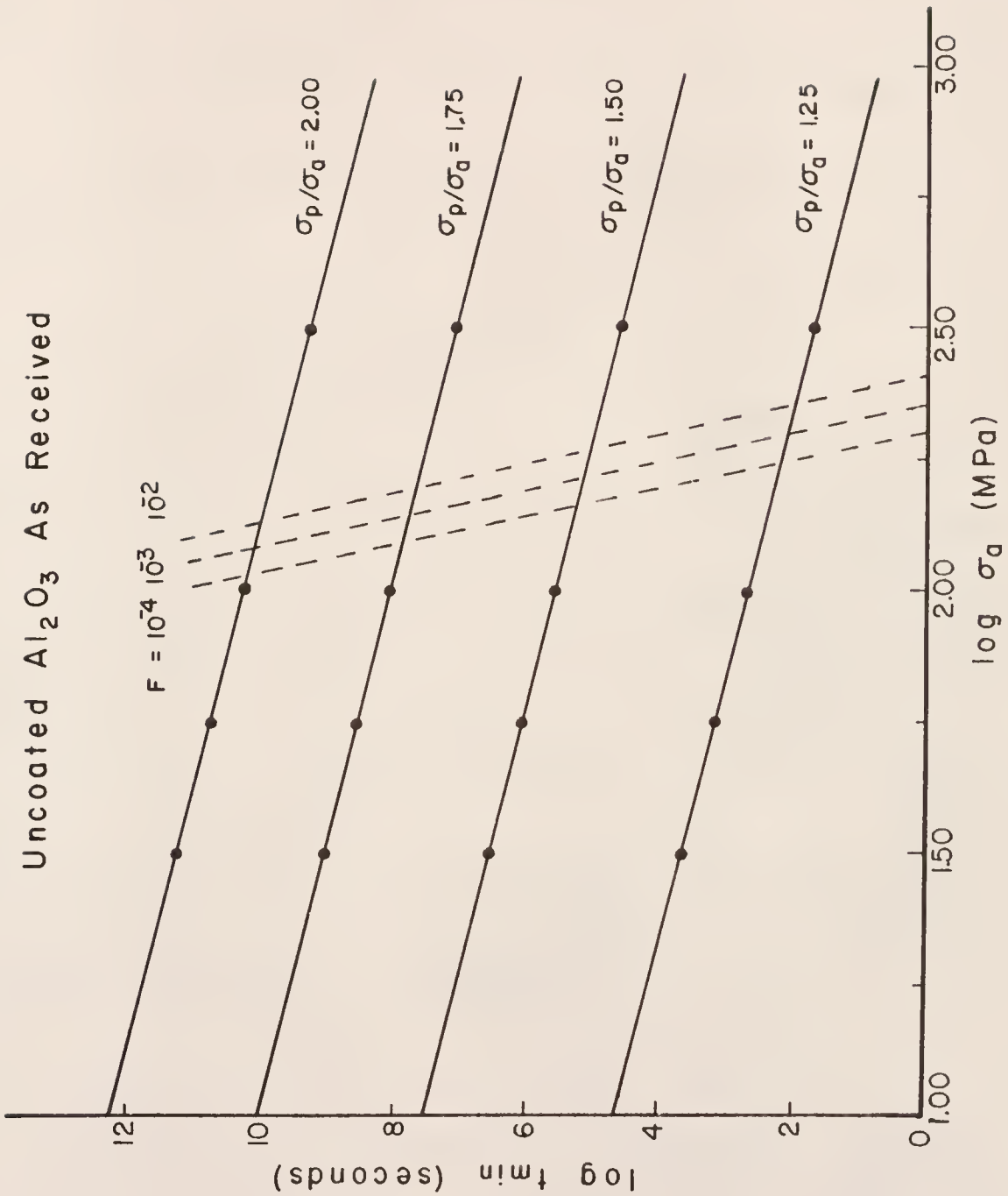


Figure 42. Lifetime prediction diagram for double-coated alumina,
tested in tris buffer.

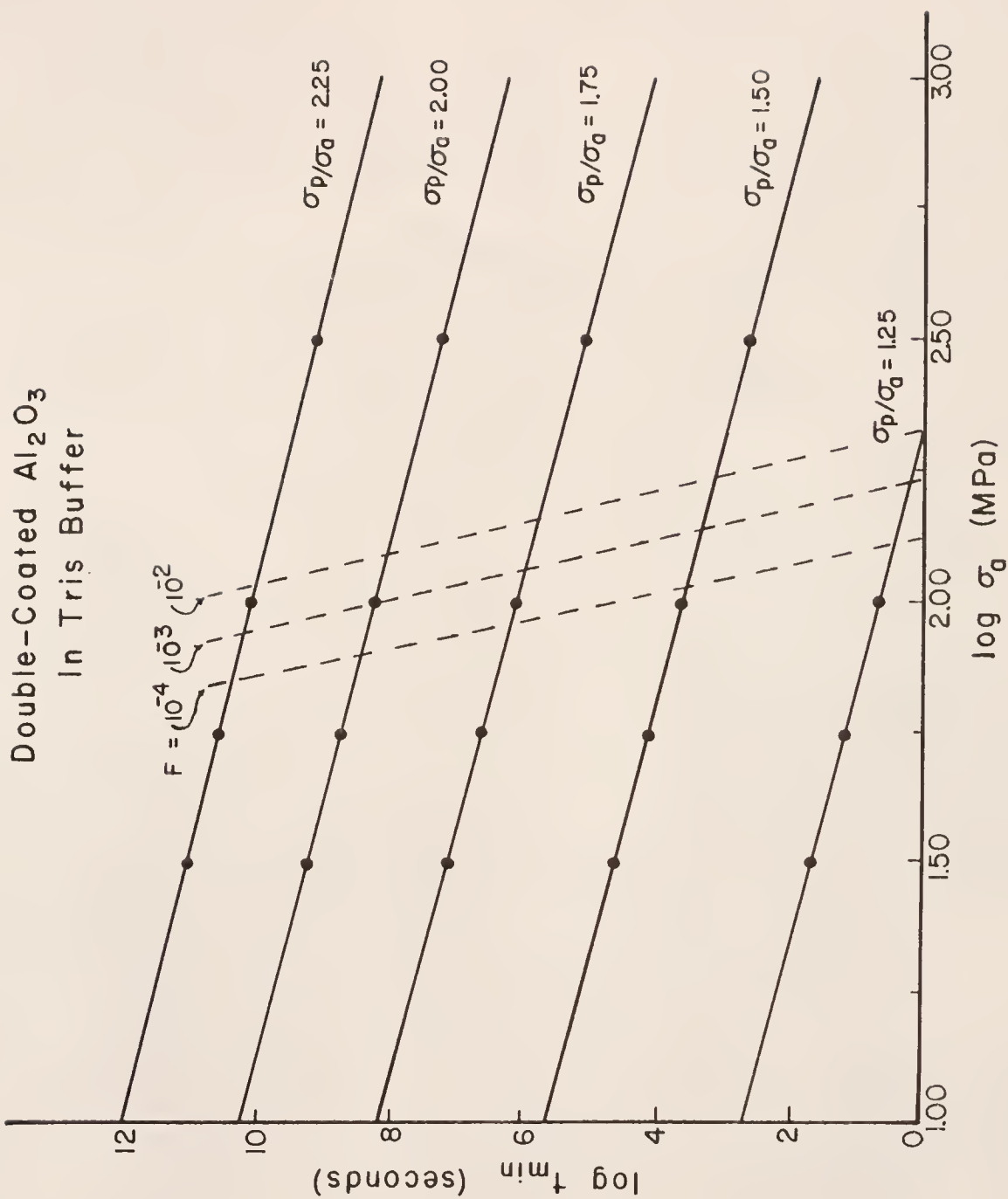


Figure 43. Lifetime prediction diagram for uncoated alumina,
tested in tris buffer.

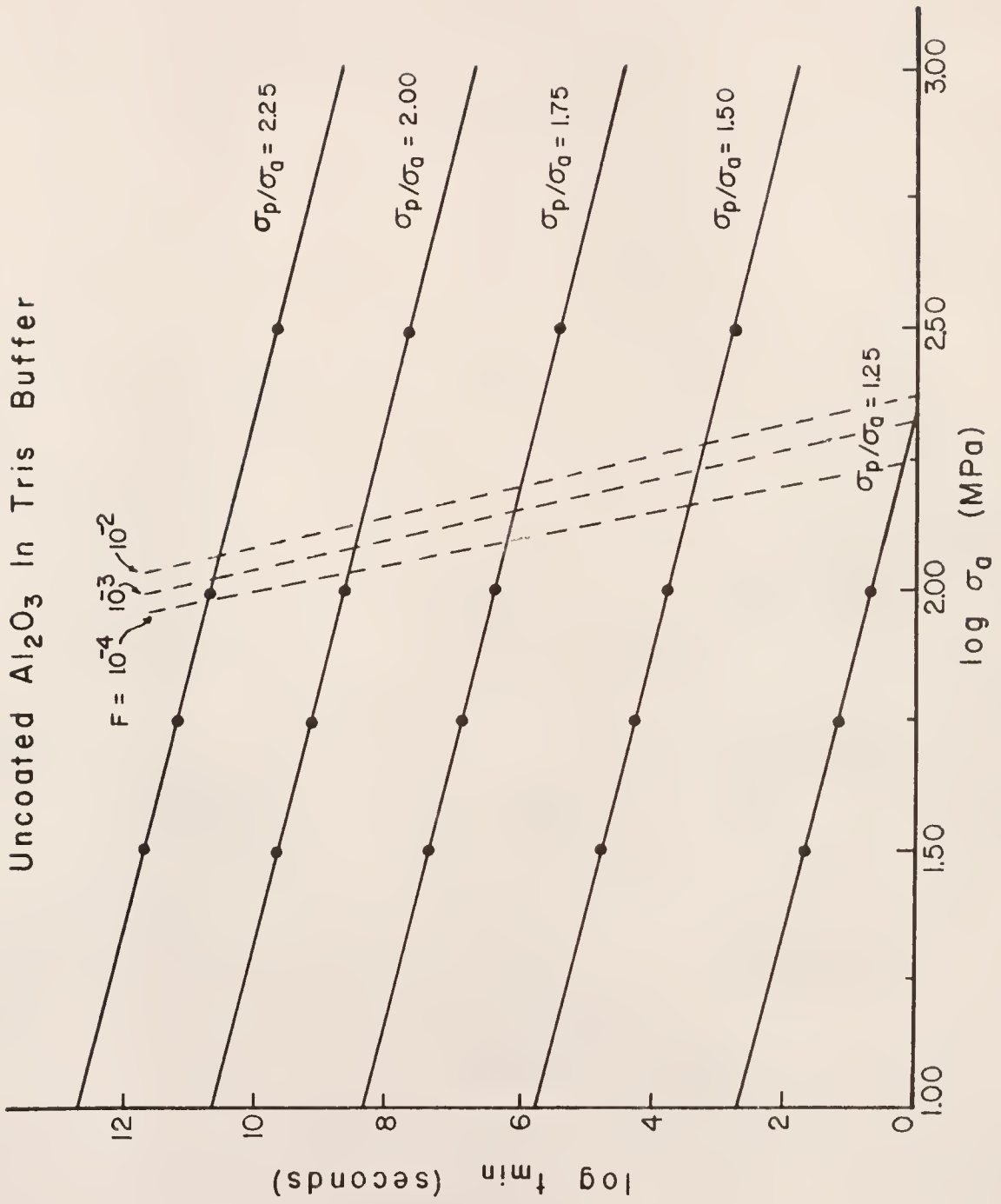


Table 9
Crack Growth Parameters and Proof Test
Stress Ratios for Coated
and Uncoated Al_2O_3

	<u>log B</u>	<u>N</u>	<u>σ_p/σ_a</u>
Al_2O_3 as received	3.1189	39	1.79
Al_2O_3 in tris buffer	0.9619	41	1.98
Coated Al_2O_3 as received	3.3016	34	1.94
Coated Al_2O_3 in tris buffer	1.1189	39	2.03

$10^{8.49}$ seconds (10 years). The results show a somewhat higher σ_p/σ_a ratio for the double-coated alumina. From these data, it is apparent that the double-coated alumina must be tested at a higher proof test stress than the uncoated alumina to ensure the same lifetime for the same given service stress.

The failure probability lines (dashed lines on the lifetime diagrams) were calculated according to Equation (7). Assuming a given t_{min} and σ_a as above ($10^{8.49}$ seconds, 104 MPa), it is clear that the probability of failure for the coated alumina is slightly greater than for the uncoated alumina. The Weibull modulus, m , in Equation (7) is a measure of the strength distribution of a given set of data. A low value of m indicates a material containing flaws of high variable severity, while a high value of m indicates a material with a uniform flaw distribution. Calculation of m for coated and uncoated alumina have been carried out. These results show a higher m value for uncoated alumina. This means that uncoated alumina has a narrower range of strength distribution. This difference in strength distributions explains the results obtained for the various probability values (e. g., the coated alumina system has a higher probability of failure with proof testing to eliminate weak samples).

The results of proof testing are summarized in Table 10. The results show that within the predicted

Table 10
Results of Proof Testing

Number of Samples	σ_p	σ_a	$t_{min.}$ (minutes)	Number Failed
	Uncoated Al_2O_3			
8	250	200	1.75	0
Double-Coated Al_2O_3				
8	210	150	5.0	0

Inert Strength of Double-
Coated Al_2O_3 After Proof Testing

$$\bar{x} = 405$$

$$\sigma = 39$$

$$\sigma/\bar{x} = 9.6\%$$

$$n = 11$$

$$\text{Weibull modulus} = 9.68$$

$t_{\min}$ at the applied stress given, no samples failed. This fact was found to hold true for both the coated and uncoated alumina samples. All 16 samples were held at the service stress for 15 minutes, at which time the tests were discontinued. No samples failed within the 15 minutes of the test. To assure that no damage was introduced to the samples by the proof test, a separate group of 11 double-coated alumina samples was given a proof test at a stress of 220 MPa and then fractured in liquid N_2 . The results presented in Table 10 show that no strength degradation has occurred. The fact that the Weibull modulus, m , has not changed is proof that the strength distribution did not change. This is further evidence that proof testing is in no way damaging the samples.

Summary

The results of the cyclic fatigue testing showed that the coating of bioglass onto alumina appeared to increase the fatigue resistance of the alumina at high stress levels as indicated by the shifts in the average number of cycles to failure to higher values for double-coated samples. Furthermore, the increase in temperature from 22° C to 37° C had no effect on the endurance limit of either the coated or uncoated alumina. There was no adverse effect of the simulated physiologic buffer

on the endurance limit of the coated and uncoated system. Finally, an endurance limit of 193 MPa (28,000 psi) was found for both coated and uncoated alumina. This limit, obtained at 10^7 cycles was found to be 65% of the flexural strength of the material. These data, presented in Table 11, agree favorably with much of the published data on alumina.

Results of the in-vivo aging tests showed a 18% decrease in the strength of the double-coated alumina. Tests conducted in-vitro under nonloaded conditions showed the same decrease in strength as the in-vivo results. Uncoated alumina samples aged in-vitro showed a slightly higher decrease in strength. Thus, the decrease in strength observed under nonloaded conditions was less than that under cyclic loading. Furthermore, while the state of stress of the in-vivo samples cannot be precisely determined, it is clear from the data that the stress conditions in the dog fibulae were not as severe as those found in cyclic loading.

The results of the stressing rate experiments clearly show that the coated alumina system has a higher fracture strength than the uncoated alumina. The fact that this increase in strength was not due to residual stresses in the material was demonstrated by testing in two different inert atmospheres, at two different temperatures. Furthermore, comparison of

Table 11

Summary of Fatigue and Delayed Failure Data
for Various Polycrystalline Aluminas

Al_2O_3	Flexural Strength (Short Term Strength)	Static Fatigue Limit	Cyclic Fatigue Limit	Ref.
99.5%	265 MPa	199 MPa	----	1
99.0%	255 MPa	200 MPa	145 MPa	2
99.5%	241 MPa	172 MPa	----	4
99.0%	280 MPa	----	193 MPa	Present Work

Figures 38 and 39 showed that the fracture strength of coated alumina decreased less in tris buffer than did the uncoated alumina.

The results of calculations of the crack growth parameters B and N showed differences between coated and uncoated alumina. In addition, these values were found to change systematically when tested in solution. From these data, in combination with the strength data, it can be concluded that the coating process has in some way changed the material. It seems most likely that the change in B from uncoated to coated alumina is due to an alteration of the strength determining flaws in the system (i. e., the surface flaws). Changes in the flaw geometry or flaw size, should lead to the observed increase in fracture strength.

Further evidence that the coating process has altered the strength determining flaws in the alumina has been gained from the lifetime prediction diagrams, along with statistical analyses of the strength distributions of both coated and uncoated alumina. The Weibull modulus has been shown to decrease from a value of 20 for uncoated alumina to a value of 10 for double-coated alumina. This decrease in m represents a wide range in the strength distribution of the double-coated alumina. This increase in the range of the strength distribution explains the necessity for a

higher σ_p/σ_a for the coated alumina. Although the coated system has a higher average flexural strength, the probability of finding an extremely weak sample is also greater. However, it also indicates that if improvements in processing can be achieved to increase m to a value comparable to uncoated alumina, a considerable improvement in service lifetime for the coated system should be realized.

Finally, the utility of the lifetime prediction diagram has been demonstrated. Standard cyclic fatigue testing used in this study has shown almost no difference between the behavior of the coated alumina system and the uncoated system. In contrast, the process of constructing lifetime diagrams has shown up differences between the coated and uncoated systems, both in the strength distribution of the two materials and in the overall strength of the coated and uncoated alumina. It has also given an indication as to the direction for accomplishing important improvements in total performance; i. e., alter processing to increase the Weibull modulus.

CHAPTER V

IMPLANT PROPERTIES OF BIOGLASS-COATED ALUMINA

Introduction

The previous chapters in this work have presented a large number of laboratory techniques used to develop and monitor the bioglass-coated alumina system. However, it is apparent that the most important property of the material is its in-vivo response. The ability of bone to bond with bioglass-coated alumina will largely determine its usefulness as an orthopaedic or dental implant system. In addition, the bone-bonding ability of the coated alumina will also aid in establishing the practicality of the in-vitro techniques used in this study to develop the system.

In this work, the 45S5 bioglass composition was again used as a point of reference in evaluating the behavior of the bioglass-coated alumina system. There has already been extensive work done on evaluation from standard histology of the bone-bioglass interface [17-21], to mechanical evaluation of the bone-bioglass bond [51, 68, 69]. The study of the interfacial bond has also included the use of Auger electron spectroscopy

(AES) and scanning electron microscopy (SEM) techniques. Each technique has contributed in some way to understanding the mechanisms, rate and strength of the bone-bioglass bond [68-71].

The use of high density alumina in this study has prevented the application of standard histologic procedures to analyze the glass-bone interface. This problem is due to the fact that the Al_2O_3 substrate is a harder material than a standard glass histologic microtome knife. The expense and delicacy of diamond knives have prevented their use for preparation of the glass-coated alumina system. Therefore, the in-vivo response of the glass-coated alumina will be evaluated by the use of mechanical testing of the bond, along with SEM-EDX analysis of post in-vivo implants.

Procedures

Rat Tibial Model

Both single and double glass coatings on 99% Al_2O_3^* were processed as described in Chapter II. The revised firing schedules presented in Table 3 of Chapter II were followed in producing the coated alumina samples. The rectangular implants which were 4 mm x 4 mm x 1 mm, were ultrasonically cleaned in acetone for

*99% Al_2O_3 , Friedrichsfeld, GmbH, Mannheim, Germany.

two minutes to remove superficial contaminants after coating. The samples were gas sterilized and implanted into defects made across the anterior border of the tibia of Sprague-Dawley rats weighing between 250-300 gr. The bony defect was made just distal to the epiphysial plate using a Hall II* drill with a 0.7 mm carbide tip. Care was taken that a close fit without excessive clearance was obtained.

Implants were retrieved after 10 days, 21 days, 30 days, 6 weeks, 12 weeks, 6 months, and 1 year. One series of single-coated alumina rat chips were prepared for standard histology after sacrifice. The tibiae were dissected clean of soft tissue and the section of bone containing the implant fixed in cold cacodylate buffered gluteraldehyde for two hours. The specimen was rinsed with fresh buffer and then dehydrated in mixtures of graded alcohol and propylene oxide, and embedded in Epon 812. The block was then either cut with a diamond wafering blade or fractured and prepared for SEM observation.

The other series of both single and double-coated alumina were subjected to a push-out force using a test method developed specifically for this implant model [51]. At sacrifice the tibiae were excised and the soft tissue surrounding the implant carefully removed. Modified sponge forceps were used to apply push-out

*Zimmer, U.S.A, Warsaw, Indiana.

loads up to 30 N. Those implants which withstood this push-out force were classified as having passed this test. Those implants which were found to move at a load less than 30 N were classified as failures.

After the push-out test was performed, those samples which passed the test were placed in cacodylate buffered gluteraldehyde and subsequently dehydrated in graded acetones. The samples were then transferred to a critical point drying apparatus.* The critical point of CO₂ was used to dry the samples. The dried tissue was then fractured and the fracture surfaces prepared for SEM-EDX investigation.

Canine Model

Right circular cylinders of 99% alumina 6 mm dia. x 12.5 mm long were single-coated with the 45S5 composition as previously described. In addition to the single-coated alumina, bulk bioglass (45S5), uncoated alumina, 316 L stainless steel,** and Wrought Cobalt Chrome Surgical Alloy*** were also used.

Implantation was carried out using techniques as described by Nilles et al. [72]. Implants were gas sterilized and inserted into transverse holes drilled in the lateral cortex of the femurs of mongrel

*Tousimis, Inc., Rockville, Maryland.

**Zimmer, U.S.A., Warsaw, Indiana.

***Vitallium - Howmedica, Rutherford, New Jersey.

dogs weighing 20-30 kg. Sterile surgical procedures were followed for all implantations. At 16 weeks the animals were sacrificed and the femurs were sectioned to form individual test pieces. The bones were kept moist throughout processing using saline solution.

A self-aligning test fixture was fabricated to ensure purely axial loading of the specimens. The fixture was mounted in a universal testing machine* and the specimens were loaded at a rate of 0.05 in./min.

Results and Discussion

Single-Coated Alumina

Results of the first series of rat tibial implants are presented in Table 12. A total of four implants were used for each time period, three being single-coated alumina, the control being uncoated alumina. The abbreviations used in Table 12 are qualitative descriptions of the resistance of implants to removal from the implant site. The notations mean: 1) N.A. = no attachment of the implant to bone was found, 2) M.T. = mechanically tight, e. g., the implant was fixed in the site but could be pried loose by hand, 3) ATT. = attached, e. g., the implant was firmly attached to bone and could not be loosened by hand,

*Instron Corp., Greenville, North Carolina.

Table 12

In-Vivo Results of Single-Coated Alumina vs.
Uncoated Alumina Implants

Time	Uncoated Al_2O_3	Coated Al_2O_3	Coated Al_2O_3	Coated Al_2O_3
10 Days	N.A.	M.T.	N.A./N.B.	N.A.
23 Days	N.A.	ATT./N.B.	N.A.	N.A.
6 Weeks	ATT.	ATT./N.B.	M.T./N.B.	M.T.
12 Weeks	N.A.	ATT./N.B.	ATT.	Infection
6 Months	N.A.	ATT./N.B.	ATT.	N.A.
1 Year	M.T.	ATT.	M.T.	----

4) N.B. = new bone, e. g., evidence of new bone on the implant surface is microscopically observable.

The results presented here do show a definite trend of increased bonding of the glass-coated alumina with increasing duration of implantation. Scanning electron micrographs of one of the 6 month samples are shown in Figures 44-46. The specimen was prepared according to standard histologic procedures described in the previous section and fractured to produce the cross section as shown. Because of rapid dehydration in the sample preparation, some cracking of the bonding gel is visible (see arrow, Figures 44 and 45). However, contiguity across the interface is present in many locations. EDX analysis of region B and G of Figure 46 is shown in Figure 47. Both spectra were recorded at a magnification of 20,000 x. These data show that there is intimate contact between the bone and glass.

In comparison to these results, Figure 48 shows a cross section of an uncoated alumina rat tibial implant after 6 months. A distinct, though fairly narrow, gap between the implant (right hand portion), and the bone (extreme left) is present. This morphology was common in other uncoated specimens that were examined. It should be noted that gaps very similar to the one in Figure 48 were found upon examination of nonbonded single-coated alumina samples.

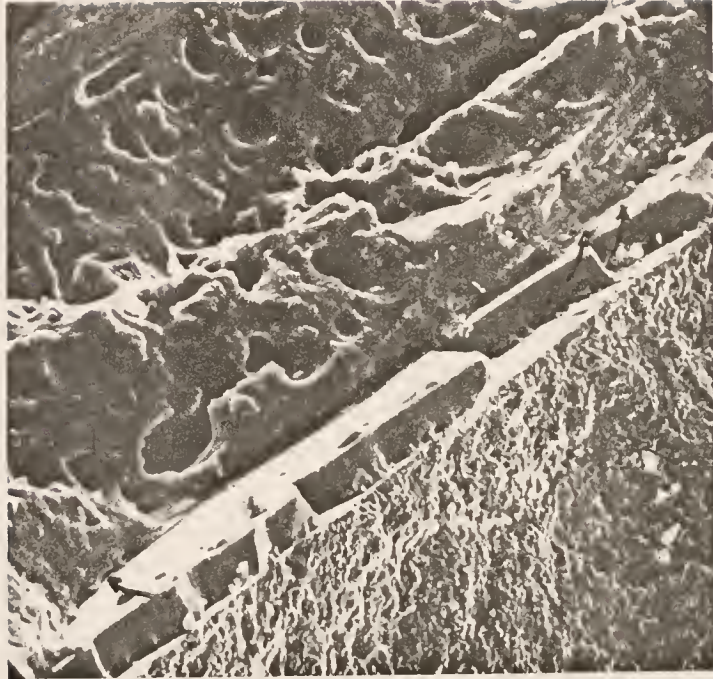


Figure 44. Morphology of a fracture surface of bone (upper left), bioglass coating (central layer), and alumina (lower right) in a 6 month rat tibial implant. (180 x)

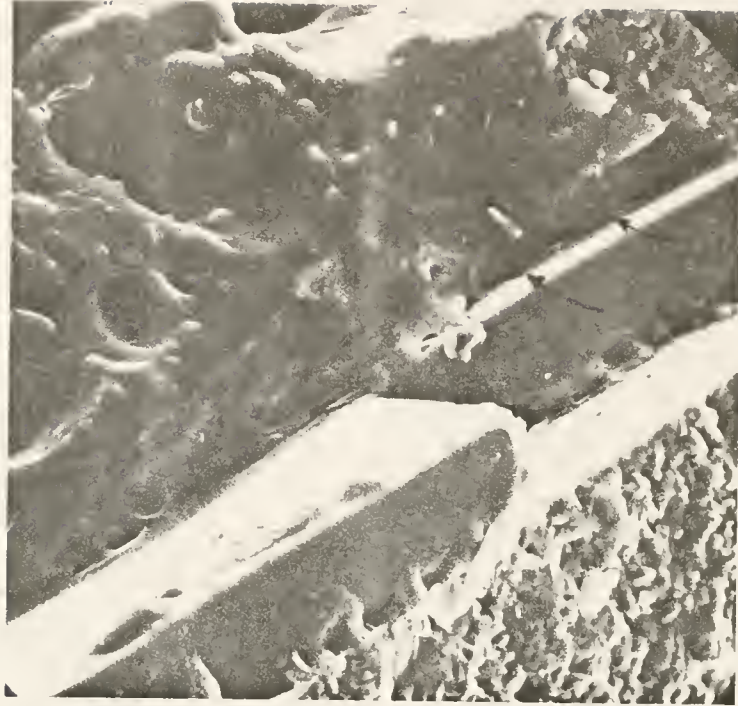


Figure 45. Higher magnification of Figure 44 showing bonding between the bone and bioglass, and the bioglass and alumina. (500 x)



Figure 46. Bone (B)/bioglass (G) interface of Figure 44 showing bonding. (2400 x)

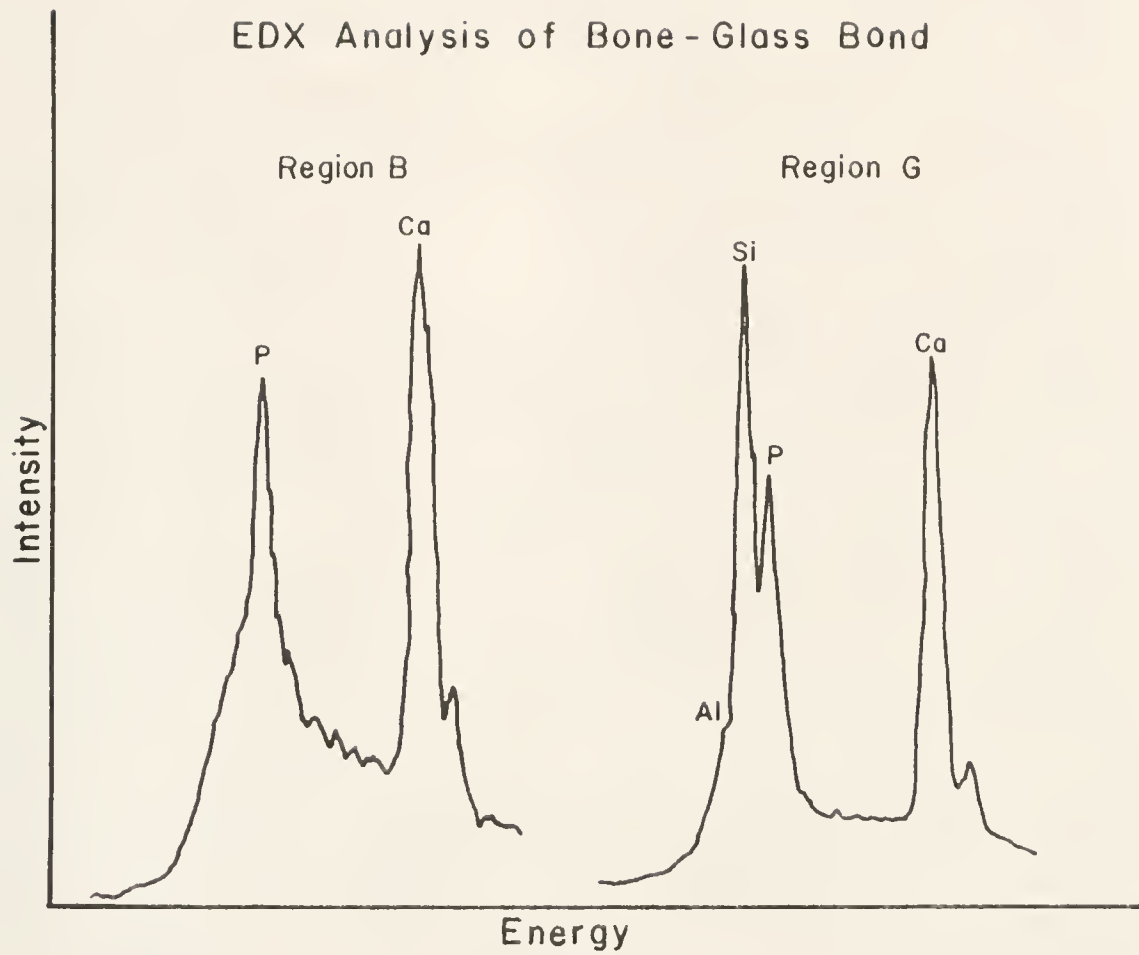


Figure 47. EDX analysis of bone-bioglass bond in Figure 46.

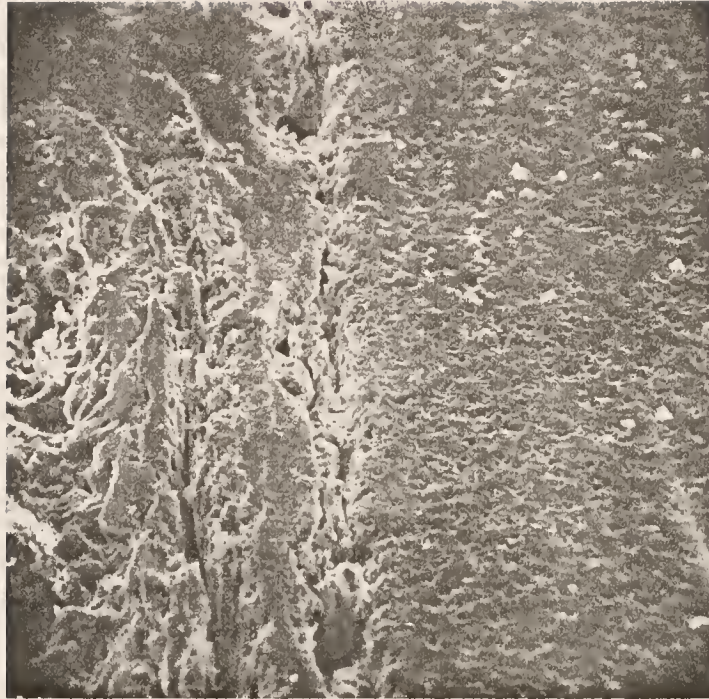


Figure 48. Cross section of an uncoated alumina-bone interface. The alumina (right side) is separated from the bone (left side) by a distinct gap running from top to bottom of the figure. (220 x)

The results of the canine push-out study are presented in Table 13. These data provide a comparison of the mechanical strength of the bone-implant bond of various materials. A statistical analysis of the data is shown in Table 14.

Comparison of the nonbonding and bonding materials showed that there was a statistically significant difference in the force to push out the nonbonding materials and the bonding materials. However, there was also a "probably significant" difference between the bond strength of the single-coated alumina and the 45S5 bioglass.

Additional information concerning the bonding of the single glass-coated alumina was obtained through the use of the "mini push-out" test described in the previous section. A comparison of the single-coated alumina vs. 45S5 bioglass in Table 15 yields some very striking results. It is immediately apparent that the single-coated alumina is nearly inert when compared to the 45S5 glass within the given time frame. In addition, the mini push-out test results are essentially in agreement with the qualitative results of Table 12.

From the results presented above it is apparent that the in-vivo behavior of single-coated alumina is very different from that of 45S5 glass. The most obvious difference between the two materials is in the

Table 13
Results of Canine Push-Out Experiment

	<u>Number of Samples</u>	<u>Mean Push-Out Force (N)</u>	<u>Standard Deviation (N)</u>
Stainless Steel 316L	5	12	13
Co-Cr Alloy	4	13	11
99% Al ₂ O ₃ (Fully Dense)	4	19	4
Single-Coated Alumina	6	61	54
45S5 Bioglass- Ceramic	15	262	117
45S5 Bioglass	5	209	92

Table 14
Statistical Comparison of Canine
Push-Out Data

Non-Bonding Materials vs. Bonding Materials

N.B. vs. 45S5 Crystallized	t=8	P>0.001	F=90
N.B. vs. 45S5	t=8	P<0.001	F=56
N.B. vs. Single-Coated Alumina	t=3.2	P<0.01	F=19

Bonding Materials vs. Bonding Materials

45S5 vs. 45S5 Crystallized	t=0.9	P>0.20	F=1.6
45S5 vs. Single-Coated Alumina	t=3.0	P<0.02	F=3.0

Note: The students "t" test assesses the significance of the difference of two means, while the "F" test compares the variances of the two groups. "P" is the probability of the two groups being represented by the same distribution.

Table 15

Summary of Rat Tibia Push-Out Data

	<u>10 Days</u>		<u>30 Days</u>	
	<u>Number Passed</u>	<u>Number Failed</u>	<u>Number Passed</u>	<u>Number Failed</u>
Single-Coated Al_2O_3	0	6	1	5*
Double-Coated Al_2O_3	0	9	10	4
45S5 Bioglass**	24	6	30	0
45S5 = 5% Al_2O_3	0	4	0	4

*One animal with broken leg not counted.

**From Reference [51].

amount of time necessary to form a stable bond to bone. The much longer time necessary for the single-coated alumina to form a bond with bone is consistent with the very low reactivity of the system observed in-vitro. The absence of a calcium phosphate film from the single-coated alumina observed in-vitro may be critical to the lack of overall bonding of the material in-vivo. Even those single-coated alumina samples which showed bonding at 6 months did not show the extensive calcium phosphate film normally associated with bulk bioglass. From these results it can be concluded that although single-coated alumina will form a bond with bone, the reactivity of the system is too low for use as a bone-bonding implant system.

Double-Coated Alumina

The results of the mini push-out test comparing single-coated alumina, double-coated alumina, and 45S5 glass are presented in Table 15. These results show a greater success rate for double-coated alumina over the single-coated alumina. However, the success rate is still below that of the 45S5 glass.

Figures 49-51 are scanning electron micrographs of a double-coated rat implant which had passed the push-out test at 30 days. The sample was dried in a critical point drying apparatus and fractured. Figure 49 shows a fracture surface of bone firmly



Figure 49. Double-coated alumina implant showing bone growing on the implant surface (Region C). (200 x)

attached to the implant. Although the origin of the cracks running through the bone cannot be precisely determined, it is likely that they are artifacts of the fracturing procedure. However, the arrows in Figure 49 point to a crack running parallel with an edge of the implant. EDX analysis of the small region devoid of bone in the central portion of the figure shows a region rich in calcium and phosphorus. This is shown in Figure 52a. The region underlying the bone is most likely the type of calcium phosphate film normally associated with 45S5 glass.

Figure 50 is an enlargement of region b in Figure 49. There is a considerable fibrous tissue, apparently growing into the implant surface. The morphology of this region is very similar to that found in 45S5 rat tibial implants after 30 days of implantation [52]. EDX analysis of this region is shown in Figure 52b. The high calcium and phosphorus levels in the spectrum indicate that the fibrous tissue might be collagen [52].

Figure 51 is a high magnification of region C in Figure 49. This region is morphologically similar to other fracture surfaces of mature bone. The EDX analysis in Figure 53 reveals only calcium, phosphorus and chlorine present. EDX analyses in other regions of the fracture surface produced the same results. As this implant had passed the push-out test, it can be concluded that this region is normal, mature bone, growing onto the implant surface.



Figure 50. High magnification of Region b in Figure 49 showing tissue growing onto implant surface. (2000 x)



Figure 51. High magnification of Figure 49 showing typical bone morphology. (5000 x)

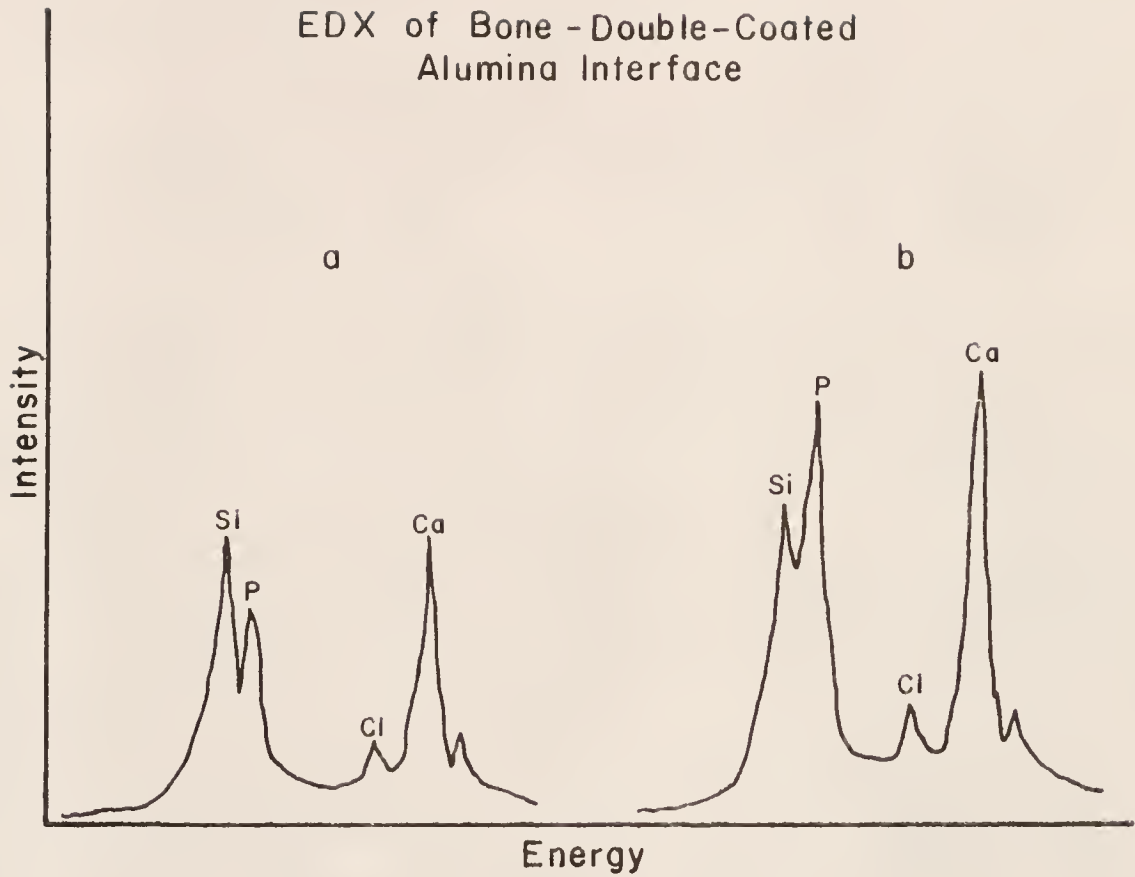


Figure 52. EDX analysis of bone-double-coated alumina interface taken from Regions a and b in Figure 49.

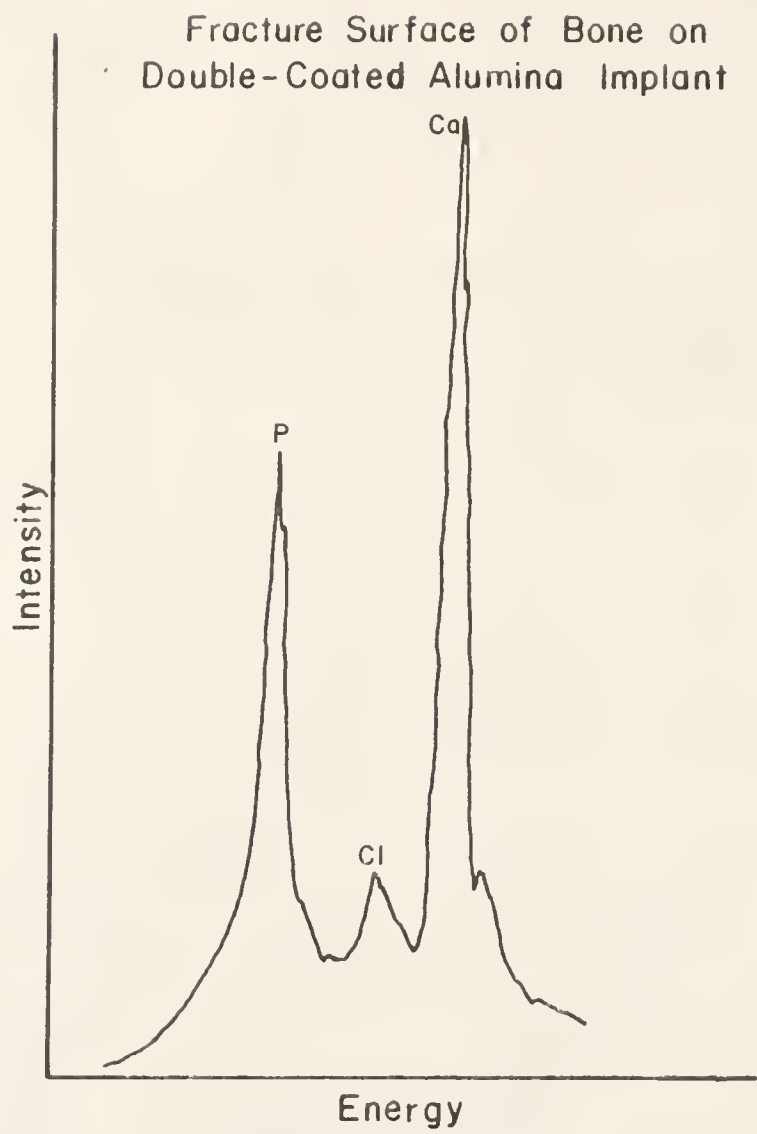


Figure 53. EDX analysis of Region C in Figure 49.

While the results above show regions of bonding very similar to that of bioglass, the push-out test does show much less reliability in the bonding of double-coated alumina as compared to 45S5 bioglass. These results are again consistent with results of in-vitro surface reactivity experiments presented in Chapter III. It will be recalled that in certain, though not all, double-coated samples, alumina was found to be present at or near the sample surface. Furthermore, it was shown that even small amounts of Al introduced into the 45S5 glass severely altered its behavior. Thus, it seems likely that the in-vivo response of the double-coated alumina should be sensitive to alumina at the surface.

Figure 54 is an EDX analysis of one of the tibial implants that failed the push-out test. It is immediately obvious that there is no calcium phosphate rich film at the surface. The presence of Al in the spectrum, and the fact that this implant failed the push-out test, supports the conclusions made in Chapter III concerning the role of alumina in the formation of the calcium phosphate film. Furthermore, these data, in combination with those presented in Figures 49-54, confirm the conclusion that the calcium phosphate film is important in the bonding of the implant to bone.



Figure 54. EDX analysis of a nonbonded, double-coated alumina surface.

Summary

The results of in-vivo testing presented in this work have shown that it is possible to form a bond between bioglass-coated alumina and bone. This result has been demonstrated in more than one animal model and with more than one type of coating. However, this work has also shown that the bonding of glass-coated alumina is, at this point in time, not as reliable as the bonding of bioglass (45S5) to bone.

Additionally, the results presented above have demonstrated that by varying the processing of the glass-coated alumina (i.e., single vs. double glass-coated alumina), a range of bondability has been achieved. Specifically, the double-coated alumina system has been shown to be more reliable in its bone-bonding ability than the single-coated alumina.

This work has also shown that the reliability of bonding can be predicted from the results of various surface sensitive, in-vitro experiments. The presence of alumina in the single-coated alumina has been shown to greatly reduce the surface reactivity of the material in-vitro. Correspondingly, there is a marked decrease in the bonding of the single-coated material to bone. The role of alumina at the surface of the double-coated alumina was also found to affect the reactivity in-vitro. This result was related to the in-vivo bondability

of the material. Where double-coated alumina implants failed the push-out test, alumina was found at the surface by EDX analysis. In contrast, no alumina was detected at the surfaces of those implants which had passed the push-out test.

Finally, the in-vivo results presented herein have shown that considerable work is still necessary to produce a bioglass-coated alumina system which can be used reliably in clinical situations. The studies dealing with processing of bioglass-coated alumina and in-vitro surface reactivity have provided the means by which reliability can be achieved. It is suggested that slight alterations in the bioglass composition will produce a surface more nearly like that of bulk bioglass, without sacrificing the ability to produce an adequate coating on alumina. The rat tibial push-out model has provided a means whereby alterations made in the coating can be screened cheaply and quickly. Using this method in conjunction with in-vitro testing procedures discussed in Chapter III, reliability in bonding should be possible.

CHAPTER VI

CONCLUSIONS

The objective of this study has been to develop a prosthetic system that will bond to bone and can be used for load-bearing applications in humans. The development of bioglass [16-20] has made it possible to achieve a direct bond between the implant material and living bone. This achievement could eliminate clinical problems of implant failure due to loosening that is normally associated with metallic prostheses. Likewise, it may make possible the elimination of in-situ polymerizing grouting agents such as PMMA routinely used in orthopaedic surgery. The use of high density alumina [13, 14] as a prosthetic device for load-bearing applications in humans has been very successful. It was felt that the combination of these two ceramic materials (i. e., bioglass as a coating on high density alumina) could provide the first implant system with the ability to bond to living bone, while maintaining adequate strength for load-bearing applications.

The first major step in the development of a bioglass-coated alumina system that will bond to bone was fabrication of the material. The results of the

processing studies showed that a diffusional bond could be developed between bioglass coatings and the alumina substrate. It was demonstrated that the diffusion of Al into the glass, and hence the tenacity of the diffusional bond, was sensitive to variations in firing time and temperature. Due to the differences in thermal expansion between the glass and the substrate, crazing of the coating was found. However, EMP studies combined with thermal expansion calculations showed that a coating with a graded thermal expansion was produced. It was concluded that the diffusion of Al into the glass coating altered the thermal expansion of the glass and was the major factor in developing a bioglass coating that was adherent to the substrate.

Results of in-vitro testing of the surface reactivity of the coated system showed that wide ranges of reactivities could be produced. The low reactivity of the single-coated alumina was found to be due to the large amount of Al present in the coating. The Al present in the glass coating was found to have a profound effect on the formation of the calcium phosphate film normally associated with reacted bioglass. Studies of bulk glass with additions of Al_2O_3 confirmed these results. Auger electron spectroscopy analysis of these glasses showed the absence of any calcium phosphate film formed on the surface. In comparison, the double-coated alumina did

develop a calcium phosphate film similar to that found on bioglass. However, this film was found to form more slowly on the coated alumina than on the bulk bioglass.

The differences in in-vitro reactivity between the single and double-coated alumina, and between coated alumina and bulk 45S5 bioglasses, were found to be consistent with the observed in-vivo bonding. Whereas bulk bioglass showed uniform bonding with good mechanical strength in many animal models, the coated alumina systems were not as reliable. The fact that the double-coated alumina was found to bond to bone more reliably than the single-coated alumina was consistent with the observed in-vitro response. Thus, a major conclusion of this work is that the analytical techniques presented in Chapter III can be used to predict the in-vivo response of a given surface active material. Furthermore, a systematic study of the in-vitro reactivity of a given system can, in turn, lead to the alteration of processing variables to elicit the desired response. Such a feedback loop developed in this study is shown in Figure 55. This feedback procedure led to the initial development of the double-coated alumina system.

Results of mechanical testing have shown that the coating process does not degrade the strength of the substrate material. This conclusion has been

Interaction Between In-Vitro Corrosion and Processing Variables

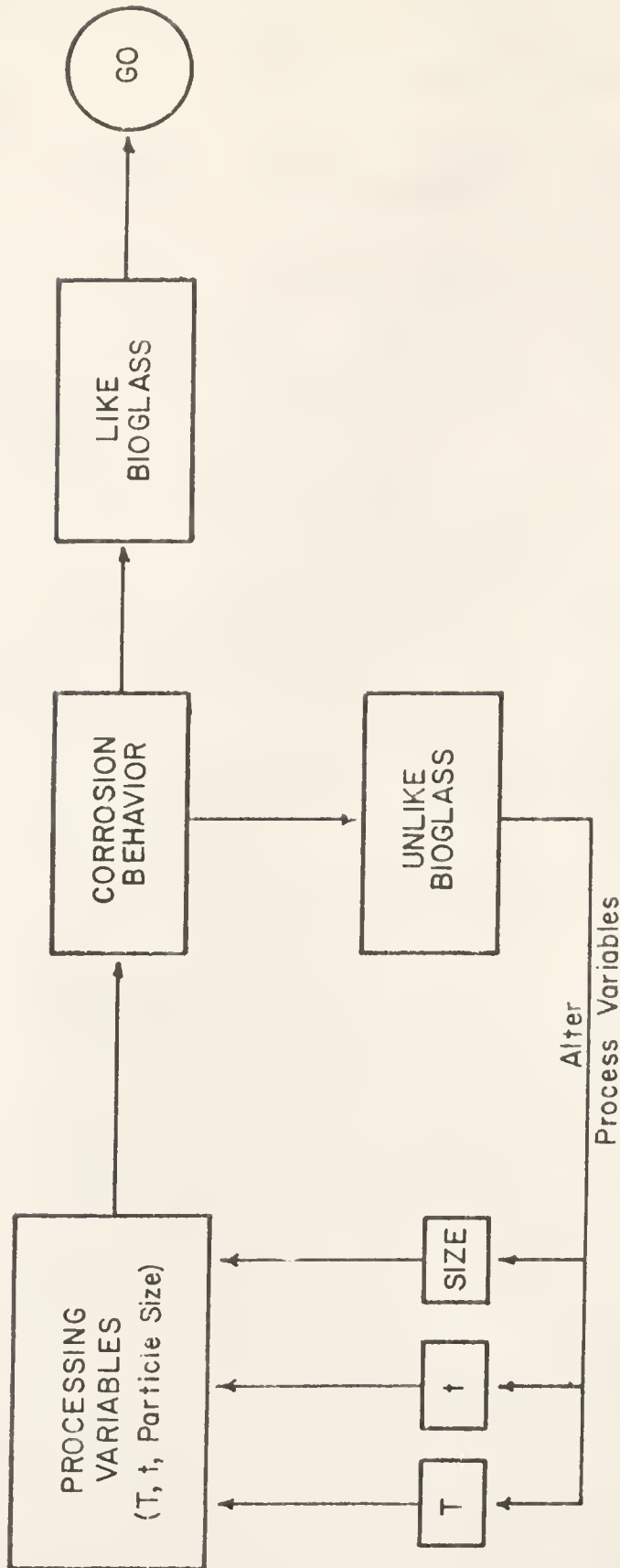


Figure 55. Feedback loop showing interaction between in-vitro response and processing history of the coated alumina system.

based on extensive cyclic fatigue testing of both coated and uncoated alumina. These tests have also shown no additional strength degradation of the coated alumina when tested in simulated physiologic solution as compared to air.

The development of lifetime prediction diagrams as a means of insuring the mechanical reliability of the glass-coated alumina has been a result of major importance in this work. The results of proof testing (Chapter IV) presented, in combination with the use of the lifetime diagrams, has shown the utility of this approach. Calculation of crack growth parameters, B and N , have demonstrated that there are differences in the mechanical properties between the coated and uncoated alumina. It is clear from these results that the coating process has altered the strength determining flaws in the alumina.

Most importantly, the results of in-vivo studies presented in Chapter V have demonstrated that bioglass-coated alumina does bond to bone. The ability of the single-coated alumina does bond to bone. The ability of the single-coated alumina to form a stable bond in rat tibiae was shown by scanning electron microscopy in histologically prepared specimens. The strength of the bond of single-coated alumina was shown to be significantly higher than either metallic implant materials or uncoated alumina. The mini push-out

test, which was developed as a screening test for the bondability of implant materials, showed a much lower success rate for single-coated alumina as compared with bulk bioglass. Thus, it can be concluded that although single-coated alumina does form a bond with bone, its reliability in bonding is very low.

By way of comparison, the double-coated alumina showed much higher reliability in bonding as determined by the mini push-out test. The differences in success of bonding between 45S5 bioglass, single and double-coated alumina was shown to be related to the alumina present in the coated system.

The utility of critical point drying in studying the bone-bioglass bond was demonstrated. The post in-vivo analysis of double-coated alumina implants by SEM-EDX showed tissue growing onto the implant surface. The tissue appeared morphologically similar to mature bone, and EDXA showed only Ca and P present. It was concluded that this tissue was, in fact, bone. Analysis of those double-coated alumina implants which failed the mini push-out test did not show such regions.

While the objective of this work has been met, it is evident that considerable work must still be done before the bioglass-coated alumina system can be used for clinical applications. The fact that the ability of the bioglass-coated alumina to bond to bone depends on the processing history of the sample provides one

means by which the system may be improved. Therefore, it is suggested that the processing variables of firing time and firing temperature be systematically altered around the processing schedule developed for the double-coated alumina in this work. Following the feedback loop in Figure 55 should lead to a better understanding of the effects of processing on the surface reactivity. This information should then be compared with results of in-vivo screening tests of new processing schedules. In this manner, an optimum coating can be developed.

There is always the possibility that the processing of the bioglass frit has altered its properties to such an extent that changes in firing schedule will not improve the bonding ability of the double-coated system. In light of recent results [73] showing a range of bioglass compositions which bond to bone, it is suggested that slight alterations in glass composition might improve the bonding reliability of coated alumina to bone. For example, slight additions of Na_2O to the glass composition would increase the surface reactivity of the system. This increase could offset the presence of alumina in the coating, thereby forming a system which will be more successful than the one described in this text.

Finally, it must be realized that the methods by which the bulk bioglass (45S5) forms a bond with bone are not yet fully understood. Until such time, it is

not reasonable to assume that all the reactions occurring in the coated alumina system will be fully understood. However, by using the techniques described in this text, and comparing the behavior of various glass coated systems with the bulk glass, considerable information concerning those conditions necessary for bonding can be obtained. This information can then be used to manufacture an optimum coating. It is hoped that this approach, in conjunction with the data base presented in this text, will lead to a greater understanding of the bonding of glass-coated alumina, as well as bioglass, to bone.

APPENDIX

The derivation of Equations (4) and (6) in Chapter IV are based on Equation (3) in Chapter IV, and are founded on the validity of the assumptions contained therein. Thus, for many ceramic systems:

$$V = AK_I^N \quad (9)$$

where K_I is the stress intensity factor, V is crack velocity, A is a geometric constant, and N is a constant related to material properties.

Under conditions of constant strain rate, $\dot{\epsilon}$, the stressing rate, $\dot{\sigma}$, is proportional to the strain rate. Furthermore, the change in applied stress, σ_a , is proportional to the differential increase in time:

$$d\sigma_a = \dot{\sigma} dt \quad (10)$$

where $\dot{\sigma}$ is the stressing rate and is load independent. From the definition of crack velocity:

$$V = \frac{da}{dt} \quad (11)$$

where a is the crack length, the total derivative of the stress with respect to crack length can be given by [63]:

$$\frac{d\sigma_a}{da} = \frac{\dot{\sigma}}{V} \quad (12)$$

As the crack velocity is a power function of the stress intensity factor, Equation (12) can be written as:

$$\frac{d\sigma_a}{da} = \frac{\dot{\sigma}}{AK_I^N} \quad (13)$$

Evans [60] has developed a relationship between stress intensity factor, applied stress, and crack length:

$$K_I = \sigma_a Y\sqrt{a} \quad (14)$$

where Y is a geometric constant. Combining Equations (13) and (14) gives:

$$\frac{d\sigma_a}{da} = \frac{\dot{\sigma}}{A\sigma_a^N Y^N \sqrt{a}^N} \quad (15)$$

Rearranging Equation (15) yields:

$$\int_{\sigma_a=0}^{\sigma_a} \sigma_a^N d\sigma_a = \int_0^{\alpha} \left(\frac{\dot{\sigma}}{AY^N} \right) \frac{1}{a^{N/2}} da \quad (16)$$

The integration of Equation (16) cannot be done directly since A and Y are functions of a . By rearranging Equation (14), it can be shown that:

$$a = \frac{K_I^2}{\sigma_a^2 Y^2} \quad (17)$$

Taking the differential of a , with respect to K_I leads to:

$$da = \frac{2K_I}{\sigma_a^2 Y^2} dK_I \quad (18)$$

Substituting Equation (17) and (18) into Equation (16) results in the integral form of the equation:

$$\int_{\sigma_a^N} d\sigma = \int \frac{\dot{\sigma}}{AY^N} \left(\frac{K_I^2}{\sigma_a^2 Y^2} \right)^{-N/2} \frac{2K_I}{\sigma_a^2 Y^2} dK_I \quad (19)$$

Combining terms yields:

$$\int_{\sigma_i}^{\sigma_f} \sigma_a^N d\sigma = \frac{\dot{\sigma}}{AY^N} \int_{K_i}^{K_{IC}} \left(2\sigma_a^{N-2} Y^{N-2} K_I^{1-N} \right) dK_I \quad (20)$$

where σ_f is the fracture stress, K_i is the initial stress intensity factor, and K_{IC} is the stress intensity factor upon failure. Thus:

$$\frac{\sigma_f^{N+1}}{N+1} = \frac{2\sigma_a^{N-2} \dot{\sigma}}{AY^2} \left(\frac{-K_i^{2-N}}{2-N} \right) \left(\frac{K_{IC}^{2-N} - K_i^{2-N}}{2-N} \right) \quad (21)$$

Since $K_{IC} \gg K_i$ and N is a large number for ceramics (~ 30), then K_{IC}^{2-N} is negligible as compared to K_i^{2-N} .

Finally, if it is assumed that:

$$\frac{\sigma_{IC}}{K_{IC}} = \frac{\sigma_a}{K_{Ii}} \quad (22)$$

where σ_{IC} is the stress at the critical stress intensity factor, K_{IC} , and K_{Ii} is the stress intensity factor for a given σ_a , then:

$$K_{IC}^{2-N} = \left(\frac{K_{IC}\sigma_a}{\sigma_{IC}} \right)^{2-N} \quad (23)$$

Substitution of Equation (23) into Equation (21) yields:

$$\sigma_f^{N+1} = \frac{2}{AY^2(N-2)K_{IC}^{N-2}} (N+1) \sigma_{IC}^{N-2} \quad (24)$$

where $\frac{2}{AY^2(N-2)K_{IC}^{N-2}} = B$ in Equation (4), Chapter IV.

Beginning with Equations (9) and (11) and setting:

$$da = Vdt \quad (25)$$

and using the relationship in Equation (18), it can be shown that:

$$\frac{Vdt}{dK_I} = \frac{2K_I}{\sigma_a^2 \gamma^2} \quad (26)$$

Substituting for V from Equation (9), and solving for dt produces:

$$dt = \frac{2K_I}{\sigma_a^2 \gamma^2 A K_I^N} dK_I \quad (27)$$

The integral form of the equation is:

$$\int dt = \frac{2}{A \sigma_a^2 \gamma^2} \int_{K_i}^{K_{IC}} K_I^{1-N} dK_I \quad (28)$$

Performing the integration, and carrying through the assumption that K_{IC}^{2-N} is negligible, and that:

$$\frac{\sigma_{IC}}{K_{IC}} = \frac{\sigma_a}{K_{IC}} \quad (29)$$

as stated above, we find that:

$$t_f = \frac{2\sigma_a^{-N} \sigma_{IC}^{N-2}}{A \gamma^2 (N-2) K_{IC}^{N-2}} \quad (30)$$

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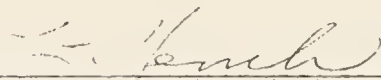
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BIOGRAPHICAL SKETCH

David C. Greenspan was born in Brooklyn, New York, on May 30, 1950. In 1968 he was graduated from James Madison High School, Brooklyn, New York. He attended Alfred University where he received a Bachelor of Science in Glass Science in June, 1972. Since obtaining his bachelor's degree, the author has been pursuing a Doctor of Philosophy in the Department of Materials Science and Engineering at the University of Florida.

He has published papers in research areas concerned with the development and processing of biomaterials and mechanical properties of ceramics. He is a member of Keramos honorary, Alpha Sigma Mu honorary, AIME, American Ceramic Society, and the Society for Biomaterials.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



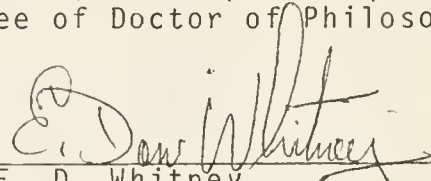
L. L. Hench, Chairman
Professor of Materials Science
and Engineering

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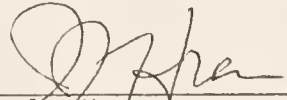
R. E. Reed-Hill
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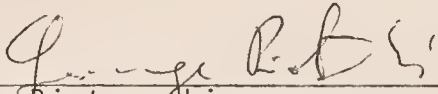
E. D. Whitney
Professor of Materials Science
and Engineering

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J. J. Hren
Professor of Materials Science
and Engineering

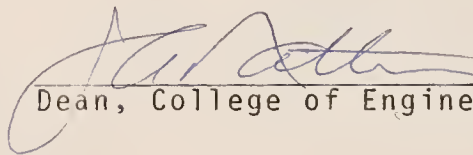
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G. Piotrowski
Associate Professor of
Mechanical Engineering

This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

~~April~~, 1977
June



Dean, College of Engineering

Dean, Graduate School

UNIVERSITY OF FLORIDA



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